

AD-A244 873



Report No. CETHA-TE-CR-90048

Comprehensive
Investigation Report

USATHAMA

U.S. Army Toxic and Hazardous Materials Agency

**TECHNOLOGY EVALUATION FOR
TREATMENT/DISPOSAL OF
TNT RED WATER**

(TASK ORDER NO. 2, SUBTASK NO. 3)

April 1990

Contract No. DAAA15-88-D-0001

Prepared by

PEI Associates, Inc.
11499 Chester Road
Cincinnati, OH 45246

DTIC
ELECTE
JAN 17 1992
S B D

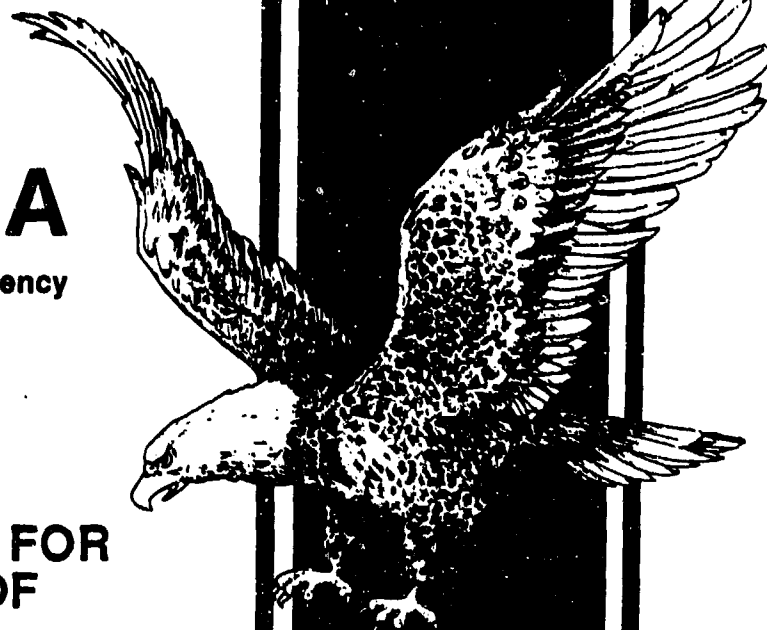
DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

Prepared for

U.S. Army Toxic and
Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010-5423

DISTRIBUTION UNLIMITED



92-01435

210 97 7 90

TECHNOLOGY EVALUATION FOR
TREATMENT/DISPOSAL OF TNT RED WATER
Comprehensive Investigation Report

by

PEI ASSOCIATES, INC.
11499 Chester Road
Cincinnati, Ohio 45246

Contract No. DAAA15-88-D-0001
Task Order No. 0002
Subtask No. 3
PN 3769-2-C

Ms. Janet Mahannah
Project Officer

for

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MARYLAND 21010-5423

April 1990

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION <u>Unclassified</u>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			Unlimited		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION		
		N/A	U.S. Army Toxic and Hazardous Materials Agency		
6c. ADDRESS (City, State, and ZIP Code)			7b. ADDRESS (City, State, and ZIP Code)		
			ATTN: CETHA-TE-D Aberdeen Proving Ground, MD 21010-5401		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
U.S. Army Toxic and Hazardous Materials Agency		CETHA-TE-D	Contract DAAA-15-88-D-0001 Task Order No. 0002 Subtask No. 3		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
ATTN: CETHA-TE-D Aberdeen Proving Ground, MD 21010-5401			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification)					
Technology Evaluation for Treatment/Disposal of TNT Red Water					
12. PERSONAL AUTHOR(S)					
John A. Wentz, John E. Spessard, Judy Hessling, Mike Resch, Janet Mahannah					
13a. TYPE OF REPORT		13b. TIME COVERED		14. DATE OF REPORT (Year, Month, Day)	
Final		FROM 10/88 TO 11/89		April 1990	
15. PAGE COUNT					
322					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Red water- Wet air oxidation		
			TNT purification Red Water incineration		
			TNT wastewater Circulating bed combustion		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>Red water is the wastewater resulting from the purification of TNT, which, because of its reactivity, is listed as a K047 waste by RCRA. A lack of suitable treatment/disposal options for the generated red water affects both plants that produce peace-time quantities of TNT and those that would be mobilized in the event of military conflicts. Extensive efforts have already been expended on the evaluation of technologies for the treatment of red water. A portion of these efforts culminated in an April 1980 report issued by Chemical Systems Laboratory (CSL), in which 10 technologies were evaluated based upon their technical merit for treatment of red water. The evaluation concluded that three technologies were technically feasible, but that two of these involved a change in the TNT purification process, which would present unwanted ramifications regarding handling and usage in the TNT specifications. Based upon these conclusions, the U.S. Army pursued the one recommended treatment technology for implementation at the Radford Army Ammunition Plant. Because of various developments, the U.S. Army, through the U.S. Army Toxic and Hazardous Materials</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT			21. ABSTRACT SECURITY CLASSIFICATION		
<input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL
Janet Mahannah			(301) 671-2054		CETHA-TE-D

18. Subject Terms (cont.)

Slagging rotary kiln
Submerged combustion

19. Abstract (cont.)

Agency, elected to perform an updated technology evaluation to reevaluate the technologies evaluated in 1980 and to determine whether processes developed since 1980 might be feasible for red water treatment.

Thirty technologies were initially evaluated against a set of preliminary evaluation criteria, which reduced the number to 16. Ultimately, only 14 technologies were subjected to a secondary set of evaluation criteria to identify and prioritize the technologies for red water treatment. The four technologies that emerged with the greatest potential for red water treatment are wet air oxidation, circulating-bed combustion, slagging rotary kiln, and submerged combustion. It is recommended that use of an already permitted existing industrial technology be evaluated as a potential short-term treatment/disposal option for RAAP-generated red water while further investigations into the suggested technologies are conducted.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAA15-88-D-0001, Task Order No. 2, Subtask No. 3, to PEI Associates, Inc. It has been subjected to the Agency's peer and administrative review and has been approved for publication as a USATHAMA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

STATUS

This document represents the ongoing evaluation of technologies for the treatment/abatement of TNT red water. This document supersedes the "Technology Evaluation for Abatement of TNT Red Water, Interim Report No. 1, Go/No-Go Evaluation," dated May 1989.

DISPOSITION

Destroy this report when it is no longer needed. Do not return it to the originator.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

PREFACE

The U.S. Army is contemplating starting up one or more of its currently mothballed trinitrotoluene (TNT) production plants. The objective is to provide an economically competitive domestic source of TNT. A requirement of startup is that the production waste stream (red water) be treated in a safe acceptable manner that complies with applicable Federal and State regulations.

In April 1980, the U.S. Army Chemical Systems Laboratory (CSL) prepared and submitted a report that summarized the more promising processes then available for the treatment of TNT red water. These processes had been studied by Large Caliber Weapons Systems and Laboratories, Radford and Volunteer Army Ammunition Plants, U.S. Army Mobility Equipment R&D Command (MERADCOM), U.S. Army Natick R&D Command (NARADCOM), and Naval Surface Weapons Command (SWC), as well as through contracts with private industry. This report is a follow-on to the 1980 CSL study and presents a compilation of previously gathered information concerning technologies for red water treatment and the results of the investigations of newer technologies that have emerged (or matured) since the 1980 CSL report.

This report provides a summary review of all of the technologies (previously evaluated or newly emerging) potentially available for treatment of red water produced during the manufacture of TNT. This study represents the most recent efforts by the U.S. Army to identify the optimum red water treatment process. The highest rated technologies are recommended for more detailed evaluations and possible laboratory and pilot-scale testing.

This report was authorized by the United States Army Toxic and Hazardous Materials Agency, Contract No. DAAA15-88-D-0001, Task Order No. 2, Subtask No. 3. Technical investigations and report preparation were performed during the period of October 1988 to December 1989.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the USATHAMA, Aberdeen Proving Grounds, MD 21010. The Defense Technical Information Center, however, is authorized to reproduce this document for U.S. Government purposes.

SUMMARY

The U.S. Army is continuing their investigation of potential processes for treating or disposing of the process waste stream (red water) resulting from TNT production and purification.

Thirty technologies for treating red water were proposed for evaluation by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and PEI Associates, Inc. (PEI). The preliminary evaluation used a decision tree to determine the potential of each process to provide a technically, economically, and environmentally acceptable method for disposing of waste products from the purification of crude TNT.

After the preliminary evaluation, 14 technologies were identified for secondary evaluation. The secondary evaluation used several criteria and a point assessment scale to identify the following four processes for further evaluation:

- 1) Wet air oxidation
- 2) Circulating-bed combustion
- 3) Slagging rotary kiln
- 4) Submerged combustion

Wet air oxidation involves oxidation with air or oxygen at temperatures between 175° and 327°C (347° to 621°F) and pressures between 2,069 to 20,690 kilopascals (300 to 3,000 psig). The advantages are a one-step operation with an estimated installed cost of \$2.5 million. Prior experiments with red water demonstrated that a 96 to 97 percent reduction of the chemical oxygen demand was achieved, which produced a virtually colorless effluent. If the effluent can be delisted as a hazardous waste and treated in a conventional wastewater treatment plant, the technology has potential; however, the effluent composition has not yet been identified.

Circulating bed combustion involves thermal treatment of wastes at temperatures between 800° and 1000°C (1472° and 1832°F). The principal difference between CBC and the more traditional fluidized-bed incineration

technologies is that CBC involves the introduction of air at much higher velocities, which causes waste particulates to be suspended in the combustion gases. These highly turbulent conditions promote efficient combustion of organics, which reduces the required residence times. Full-scale CBC systems are in operation for solids. Full pilot-scale demonstrations have been successfully completed on liquid wastes. Pilot-scale facilities are currently available where red water treatment efficiencies and ash characteristics could readily be performed. Completion of pilot-scale tests on red water could be realized within 1 year with approximate costs ranging from \$60,000 to \$250,000, depending on the exact nature of the test and analytical requirements.

Incineration by slagging rotary kiln is a process in which wastes are incinerated in a rotary kiln at temperatures greater than those used in standard rotary kilns. The slagging rotary kiln generally operates between 1100° and 1300°C (2012° and 2372°F), which results in the generation of slag and combustion gases. The higher temperatures of the process enable a more complete combustion of the wastes and encapsulation of constituents in the generated slag. Sufficient temperatures would be maintained to melt the salts contained within the red water, which would then be removed from the kiln in liquid form. The generated slag from the slagging rotary kiln has been determined to be much more resistant to leaching than ash produced from standard incineration processes. The slagging rotary kiln is in full-scale operation in Europe and the United States. The technology has been used effectively for more than 10,000 types of wastes with removal efficiencies of greater than 99.99 percent for most compounds tested. Time and cost are relatively low because of the extensive experience already acquired with the slagging rotary kiln process. Pilot-scale studies are estimated to last 2 to 6 months and cost from \$10,000 to \$200,000, depending on the extent of the testing performed.

The submerged combustion process is similar to the slagging rotary kiln in that higher temperatures are maintained to melt the salts and to produce a slag that encapsulates the ash constituents and thus exhibits greater resistance to leaching. The submerged combustion process is currently being used at approximately 116 different locations throughout the world. Tests on

numerous organic compounds indicate that the process is capable of achieving 99.99 percent reduction; however, no pilot-scale tests of the submerged combustion process could be performed in about the same timeframe and at the cost of the slagging rotary kiln.

In addition to the long-term technological processes selected, a potential short-term option was identified for red water disposal during the interim phases of long-term technology development and implementation. The short-term process involves the use of an existing industrial technology that consists of shipment of Radford Army Ammunition Plant red water to duPont's Deepwater, New Jersey, wastewater treatment plant for disposal. The duPont facility is permitted to accept K047 wastes (TNT production wastewater), and the New Jersey Department of Environmental Protection has no objection to treating Radford red water at this location.

Red water samples from the Canadian Industries Limited (CIL) TNT manufacturing plant were sent to the duPont Deepwater facility on March 14, 1990, for evaluation of treatment by the duPont process. As of the final writing of this report, teatability results had not been received.

CONTENTS

	<u>Page</u>
USATHAMA Report Documentation Page	iii
Disclaimer	v
Preface	vii
Summary	ix
Figures	xv
Tables	xv
Abbreviations and Acronyms	xvi
Acknowledgments	xviii
 1. Introduction	 1-1
1.1 Background	1-1
1.2 Present and Ongoing Process Evaluation Efforts	1-5
 2. Preliminary Evaluation of Wastewater Disposal Processes	 2-1
2.1 Technical Approach	2-1
2.2 Prescreening Decision Tree	2-4
2.3 Results of Preliminary Screening	2-6
 3. Detailed Evaluation of Wastewater Disposal Processes	 3-1
3.1 Technical Approach	3-1
3.2 Evaluation of the Technologies	3-8
3.3 Presentation of Results	3-27
 4. Recommendations	 4-1
4.1 Wet Air Oxidation	4-1
4.2 Circulating Bed Combustion	4-2
4.3 Slagging Rotary Kiln	4-3
4.4 Submerged Combustion	4-4
4.5 Proposal for Treatability Studies	4-5
4.6 Technology Treatability Evaluations With Domestic TNT Red Water and Potential Short-Term Treatment/Disposal Option for RAAP-Generated Red Water	 4-6

CONTENTS (continued)

	<u>Page</u>
References	R-1
Appendices	
A. North American TNT Plant Capacities and Properties of Radford Army Ammunition Plant Red Water	A-1
B. - NOT USED -	B-1
C. Preliminary Evaluations of Wastewater Disposal Processes; Technical Discussions and Decision Trees	C-1
D. Detailed Discussion of Candidate Red Water Treatment Technologies Surviving the Preliminary Evaluation	D-1
E. Effects of Sodium Salts on Hazardous Waste Incinerator Performance and Operation	E-1
F. Current Status of Argonne National Laboratory Process	F-1
G. Memorandum Describing Contacts Made Concerning Red Water Processing at duPont's Deepwater, New Jersey Facility	G-1

FIGURES

<u>Number</u>		<u>Page</u>
1-1	TNT Process Chemistry: Three-Stage Nitration of Toluene With Nitric and Sulfuric Acids	1-8
1-2	TNT Purification With Sodium Sulfite	1-9
2-1	Prescreening Decision Tree	2-5

TABLES

<u>Number</u>		<u>Page</u>
1-1	Technologies Evaluated in 1980 by Chemical Systems Laboratory	1-4
2-1	Technologies Selected for Preliminary Screening	2-2
2-2	Data Bases Investigated by USATHAMA and PEI in Literature Search for Information on TNT Red Water and Its Treatment	2-3
2-3	Technologies Selected for Further Evaluation	2-7
2-4	Technologies Eliminated From Further Evaluation	2-8
3-1	Wastewater Disposal Processes Receiving Detailed Evaluation	3-2
3-2	Secondary-Level Evaluation Criteria for Red Water Treatment Technology Evaluation	3-4
3-3	Comparative Evaluations of Red Water Treatment	3-28
3-4	Ranking of Evaluated Technologies in Descending Order of Qualitative Evaluation	3-29

LIST OF ABBREVIATIONS AND ACRONYMS

AAP	-	Army Ammunition Plant
AMCCOM	-	Armament Munitions and Chemical Command
ANL	-	Argonne National Laboratory
ARDEC	-	Army Research and Development Engineering Command
ARRADCOM	-	U.S. Army Armament R&D Command (1977 to 1983); changed to Army R&D Center (1983 to 1986), ARDEC (1986 to present)
ARRCOM	-	U.S. Army Armament Material Readiness Command
BATEA	-	Best Available Technology Economically Available
BRO	-	British Royal Ordinance
BV	-	Bed Volume (pertains to ion exchange)
CAAP	-	Cornhusker Army Ammunition Plant
CE	-	Corps of Engineers
CIL	-	Canadian Industries Limited
CSL	-	Chemical Systems Laboratory
CSTR	-	Continuously Stirred Tank Reactor
CWO	-	Catalyzed Wet Oxidation
DNT	-	Dinitrotoluene
DSCF	-	Dry Standard Cubic Feet
EPA	-	U.S. Environmental Protection Agency
EP TOX	-	Extraction Procedure Toxicity
ERADCOM	-	U.S. Army Electronics R&D Command
FB&D	-	Ford, Bacon and Davis
HMX	-	Cyclotrimethelene tetranitramine
HTTS	-	Hybrid Thermal Treatment System
JAAP	-	Joliet Army Ammunition Plant
LAP	-	Loading, Assembling, and Packing
LCWSL	-	Large Caliber Weapons System Laboratory
MCA	-	Military Construction, Army
MERADCOM	-	U.S. Army Mobility Equipment R&D Command
MMT	-	Manufacturing Methods and Technology

ABBREVIATIONS AND ACRONYMS (continued)

MTD	-	Manufacturing Technology Directorate
NAAP	-	Newport Army Ammunition Plant
NAP	-	Nitric Acid Purification
NARADCOM	-	U.S. Army Natick R&D Command
NAVAL SWC	-	Naval Surface Weapons Center
NJIT	-	New Jersey Institute of Technology
PAH	-	Polycyclic Aromatic Hydrocarbons
PBMA	-	U.S. Army Production Base Modernization Activity
PCB	-	Polychlorinated biphenyls
PCDD	-	Polychlorinated dibenzo-p-dioxins
PEP	-	Propellants, Explosives, and Pyrotechnics
RAAP	-	Radford Army Ammunition Plant
RBC	-	Rotating Biological Contactor
RCRA	-	Resource Conservation and Recovery Act
R&D	-	Research and Development
RDX	-	Cyclotrimethenetrinitramine
RO	-	Reverse Osmosis
SCC	-	Secondary Combustion Chamber
SRK	-	Slagging Rotary Kiln
SRP	-	Sulfite Recovery Process
SSRP	-	Sonoco Sellite Recovery Process
TCLP	-	Toxic Characteristic Leaching Process
TDS	-	Total Dissolved Solids
TNM	-	Tetranitromethane
TNT	-	Trinitrotoluene
TRP	-	Tampella Recovery Process
USATHAMA	-	U.S. Army Toxic and Hazardous Materials Agency
VAAP	-	Volunteer Army Ammunition Plant

ACKNOWLEDGMENTS

This report was prepared by PEI Associates, Inc. (PEI) of Cincinnati, Ohio, as part of the work conducted for the United States Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAA15-88-D-0001, Task Order No. 2, Subtask No. 3. Ms. Janet L. Mahannah was the USATHAMA Technical Project Monitor.

Mr. John A. Wentz served as PEI's Project Manager, and Mr. Michael E. Resch served as the Project Manager for Hunter/ESE (subcontractor to PEI). Principal authors were Mr. John A. Wentz, Dr. John E. Spessard, Ms. Judy Hessling, and Mr. Michael E. Resch. Also acknowledged are those individuals who investigated the technologies in their particular field of expertise and to Ms. Martha H. Phillips of PEI Associates, who edited the report.

We would also like to acknowledge and thank Mr. Robert E. Goldberg of the U.S. Army Production Base Modernization Activity (PBMA) and Mr. James Carrazza of the Army Research and Development Command (ARDEC), who shared their considerable expertise about previous activity in red water treatment.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Regulatory Requirements

The Federal Water Pollution Control Act, as amended in 1972 and in 1977 (the Clean Water Act of 1977), required industrial dischargers of pollutants to install, by 1984, the best technology economically available (BTEA) to protect the environment. In 1987, the Act was further amended (the Water Quality Act of 1987) to expand the Government's enforcement authority and to enact more stringent civil and criminal penalties for major violations (Brown 1987). The Water Pollution Control Act and its associated amendments maintain jurisdiction over both government and private facilities.

In conformance with these regulations, the U.S. Army began efforts aimed at pollution abatement and control. Over the years, pollution abatement has become an integral part of all U.S. Army modernization programs. In many cases, the continuing or renewed operation of facilities involved with the production, manufacturing, and handling of propellants, explosives, and pyrotechnics (PEP) depends on meeting current environmental regulations. Several Army ammunition plants already have installed pollution abatement equipment and have demonstrated successful operation.

1.1.2 Prior Disposal Methods for Wastewater From TNT Production (Red Water)

Trinitrotoluene (TNT) is not currently produced at any Army ammunition plant in the United States, partly because of the lack of treatment/disposal options for the generated wastewater (red water). Because of its reactivity, this wastewater is listed as K047 waste by the Resource Conservation and Recovery Act (RCRA). The lack of a treatment method for red water affects both plants that would produce peacetime quantities of TNT and those that

would be mobilized for an increased military need. These facilities include Radford, Joliet, Newport, and Volunteer Army Ammunition Plants.

In the production of TNT, sellite (15 percent aqueous sodium sulfite solution) is used to purify the TNT by removing all the undesirable isomers and impurities. The wastewater generated by the batch purification process contains approximately 5 percent dissolved solids, whereas the wastewater from the continuous process contains 15 to 17 percent dissolved solids. Because the wastewater generated from either process has a deep red color, it is commonly called "TNT red water."

Throughout the 1970s, red water was disposed by one of two methods: 1) evaporation to achieve 35 percent solids and sale of this concentrated red water to the kraft paper industry, or 2) incineration of the concentrated red water in standard rotary kilns. The kraft paper industry used the concentrated red water for makeup sodium and sulfur and for energy from incineration. Prior to the late 1970s, U.S. production of TNT to meet defense requirements was conducted at the Joliet Army Ammunition Plant (JAAP), where the red water was incinerated, and at the Radford Army Ammunition Plant (RAAP) and Volunteer Army Ammunition Plant (VAAP), which sold the red water to the paper industry. When the continuous TNT lines constructed at the Newport Army Ammunition Plant (NAAP) were proven out in the early 1970s, this red water was also incinerated. The imposed environmental regulations had an impact on both methods of red water disposal. The incinerators generated NO_x and particulate emissions, thus air pollution controls were required. Also, the ash was a source of leachate containing nitrobenzenes that restricted its disposal. Classification of the red water as a K047 RCRA hazardous waste restricted its shipping and treatment. Furthermore, the U.S. Environmental Protection Agency (EPA) imposed restrictions on the kraft paper industry that resulted in changes in its process. These changes eliminated the need for the concentrated red water as a source of makeup sodium and sulfur (Goldberg 1988).

1.1.3 Previous Treatment Process Development and Past Process Evaluation Efforts

In the early 1970s, methods of treating red water were investigated under a Manufacturing Methods and Technology (MMT) Project. The evaluation

was performed for red water generated at VAAP (second largest U.S. Army TNT manufacturing plant in the United States; see Appendix A for information on TNT production at RAAP, JAAP, NAAP, and VAAP). In that study, the Tampella process was proposed for treatment of red water at VAAP. This process was and still is a complicated process that could be made efficient only when large quantities of red water were to be treated (Gilbert et al. 1982). When VAAP and JAAP were shut down in March 1977, domestic production of TNT by AMCCOM facilities ceased and the investigation into the Tampella process was discontinued (Goldberg 1988). Following the VAAP and JAAP TNT production line shutdowns, another red water treatment technology evaluation was performed by LCWSL in which the Sonoco Sulfite Recovery process was identified as the technology with the best potential for treatment of smaller quantities of red water. MMT subsequently initiated efforts to develop design data for implementation of the SSRP. Additionally, in 1979, anticipating the forthcoming 1984 environmental requirements and considering the smaller quantities of red water RAAP would generate to meet peacetime TNT demands, the Environmental Technology Division of the Chemical Systems Laboratory (CSL) of the U.S. Army Armament Research and Development Command (AARADCOM), under authorization of Task 1L1162720DOD48-02, prepared a report, independent of the LCWSL evaluations, discussing red water treatment technologies available at that time (Eckenrode, Denzler, and Klein 1980). This study included numerous red water treatment technologies, some of which had been proposed as early as 1971 (during the previous investigation). The report (hereinafter referred to as the CSL Report) summarized the more promising processes. A final draft of the CSL report was issued in April 1980. The report evaluated 10 separate chemical processes to determine the potential for each technology to provide a technically, economically, and environmentally acceptable method for the treatment and disposal of red water. In March 1983, after the newly constructed CIL continuous TNT production lines were tested at RAAP, RAAP became the sole producer of TNT in the United States and the quantities of red water generated at RAAP were considerably less than those generated at VAAP and JAAP.

The 1980 CSL Report has been reviewed extensively by the U.S. Army, and the results and findings presented therein have been accepted; therefore, the 1980 CSL Report has been used as the baseline for this technology evaluation. Technologies not evaluated in the 1980 CSL Report have been evaluated in a similar format to allow an objective comparison of the various technologies. The 10 technologies evaluated in the 1980 CSL Report are presented in Table 1-1.

TABLE 1-1. TECHNOLOGIES EVALUATED IN 1980 BY
CHEMICAL SYSTEMS LABORATORY

Sonoco Sellite Recovery Process
Magnesium Sulfite Purification
Nitric Acid Purification
Fluidized-Bed Reduction
Concentration followed by Incineration and Landfill
Tampella Recovery Process
Ammonium Sulfite Purification
SCA Billerud Recovery
Reverse Osmosis
Acidification

The 1980 CSL report recommended the Sonoco Sellite Recovery Process (SSRP) as the technology of choice for the treatment of red water from the RAAP TNT production lines. The report indicated that particular data gaps existed, notably concerning the furnace feed stock and actual stack emissions, and recommended that efforts be instituted to resolve them.

In 1982, a subsequent MMT Project was completed that tested key process equipment to be used in the recommended Sonoco Sellite Recovery Process. The red water used for testing was acquired from the stored inventory from earlier TNT production at VAAP. The study focused on the feed stock and actual stack emissions, as recommended by CSL. Results of the study were incorporated as changes in this phase of the Sonoco Sellite Purification Process. A sellite solution obtained from Sonoco's Hartsville, South Carolina, paper plant was used for TNT purification. The purified TNT satisfied production specifications (Helbert, Pregun, and Carrazza 1983). The

remaining portion of the process was considered identical to the Sonoco process used in the paper industry, so none of this equipment was tested. A lack of MMT funds at that time also precluded the testing of a comprehensive integrated process at any scale. The results of the MMT study formed the basis of the design criteria for a follow-on project under the Corps of Engineers' (CE) MCA Program. Management of the program was the responsibility of the Installation Support Directorate of the Armament Munitions and Chemical Command (AMCCOM) (Goldberg 1988).

In fiscal year 1985, the MCA Program was authorized with an appropriation of \$25 million, and the concept design of the SSRP treatment system was performed by Mason and Hanger, the contracted architectural and engineering firm. The contractors' bid package included the development and submittal of process equipment specifications and drawings, as required by the preliminary specifications. MCI, the successful low bidder, was awarded a construction contract in June 1985. As a result of poor performance and continuously escalating costs on this MCA project, the U.S. Army Material Command and CE jointly agreed to terminate the project. On June 7, 1988, the CE issued a termination letter to MCI (Goldberg 1988).

1.2 PRESENT AND ONGOING PROCESS EVALUATION EFFORTS

1.2.1 Objectives

The U.S. Army Production Base Modernization Activity (PBMA) submitted a Near Term Study Plan on August 1, 1988, to evaluate commercially available technologies that could be readily adapted at RAAP. The criterion was for the technology to be able to treat red water satisfactorily to meet all applicable State and Federal environmental requirements so that the U.S. Army could initiate production of TNT at the mothballed RAAP TNT production facility. The PBMA also submitted a Long Term Study Plan to evaluate advanced technologies that could be applied to the modernization of the other TNT production facilities so they would meet mobilization requirements. The PBMA Study Plan for red water treatment includes:

- ° A listing of potential red water treatment technologies to be evaluated.

- Short-term study goals and objectives.
- Long-term study goals and objectives (PEI's area of responsibility).
- Short-term and long-term objectives.

1.2.2 Objectives of the Process Evaluations

The objective of this study was to conduct a technical investigation of the technologies available or potentially feasible for the treatment and/or abatement of red water generated during TNT purification at Army ammunition plants. This represents the first stage of the Long-Term Technologies Investigations. This report describes the results of the study. Initially, 30 separate technologies were evaluated to determine their potential to provide a technically, economically, and environmentally acceptable method for disposal of waste products resulting from the purification of crude TNT. During this preliminary evaluation of 30 processes (described in Section 2), 14 processes were identified as being worthy of further consideration. Section 3 provides a more indepth investigation into the technologies surviving the preliminary evaluation, and Section 4 prioritizes and discusses the technologies recommended for further consideration by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA).

1.2.3 Red Water and the TNT Production and Purification Process

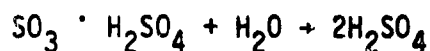
The 1980 CSL report provided a comprehensive discussion of the Canadian Industries Limited (CIL) TNT production and purification process, which is used for TNT production in all the U.S. Army Ammunition Plants. Since the 1980 CSL Report, the TNT production method has not changed with the exception that more facilities intend to convert from batch to continuous production. Most of the discussion in the following subsections concerning TNT production, purification, and the generation of red water was derived from the CSL Report.

TNT Production Process--

The U.S. Army is capable of manufacturing TNT at four locations within the continental United States. These four locations, their TNT production

capacities, and the associated quantities of generated red water are presented in Appendix A, Table A-1. Radford and Newport AAP can produce TNT by the continuous process; Joliet and Volunteer can produce TNT by either the continuous process or batch operation.

The production of TNT involves the three-stage nitration of toluene. The initial nitrating agent is a mixture of nitric acid and oleum, which is a solution of sulfur trioxide in sulfuric acid. Water is formed by the nitration reactions, and oleum is converted to sulfuric acid as shown here:



Nitric acid and oleum are more effective as a nitrating agent than are nitric acid and sulfuric acid. Adding nitro groups to the benzene ring deactivates the ring and renders further addition more difficult. Therefore, dinitrotoluene (DNT) is more difficult to form than mononitrotoluene (MNT), and trinitrotoluene (TNT) is more difficult to form than dinitrotoluene. In production processes, fresh nitric acid and oleum are used to produce TNT. This residual acid is then used to make DNT, and the residual acid from DNT production is used to make MNT. Consequently, the acid mixture and the organic compounds (toluene and nitrotoluenes) flow in opposite directions. Figure 1-1 presents a schematic of TNT process chemistry illustrating the three-stage nitration of toluene. Crude TNT is washed free of acids. This wash water, which contains nitric and sulfuric acids, is neutralized; and the resulting solution of sodium nitrate and sodium sulfate is one of the constituents of TNT or red water.

TNT Purification Process--

As shown in Figure 1-1, the predominant TNT isomer formed is the desired product, the alpha isomer or 2,4,6-TNT. About 4.5 percent of the TNT consists of unwanted isomers that must be removed. A common trait among these unwanted isomers is that at least one nitro group is in the 3 or 5 position, or the meta position. Sellite (15 percent aqueous solution of sodium sulfite) reacts preferentially with nitro groups in the meta position to form sodium dinitrotoluene sulfonate salts. These salts are water-soluble and easily separable from the water-insoluble alpha TNT. The purification

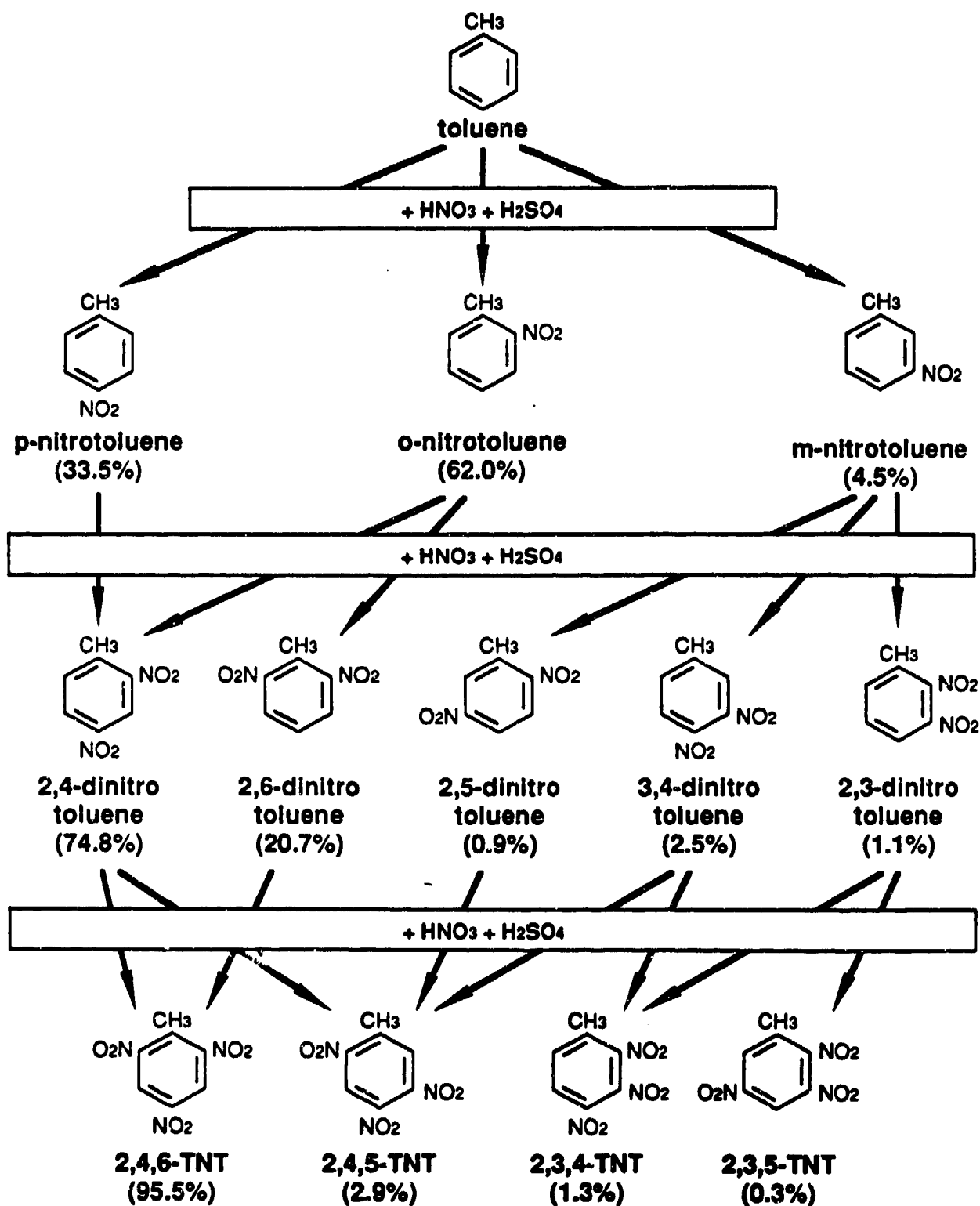


Figure 1-1. TNT process chemistry: three-stage nitration of toluene with nitric and sulfuric acids.

Source: Technical Manual for Military Explosives
TM-9-1300-214, Undated.

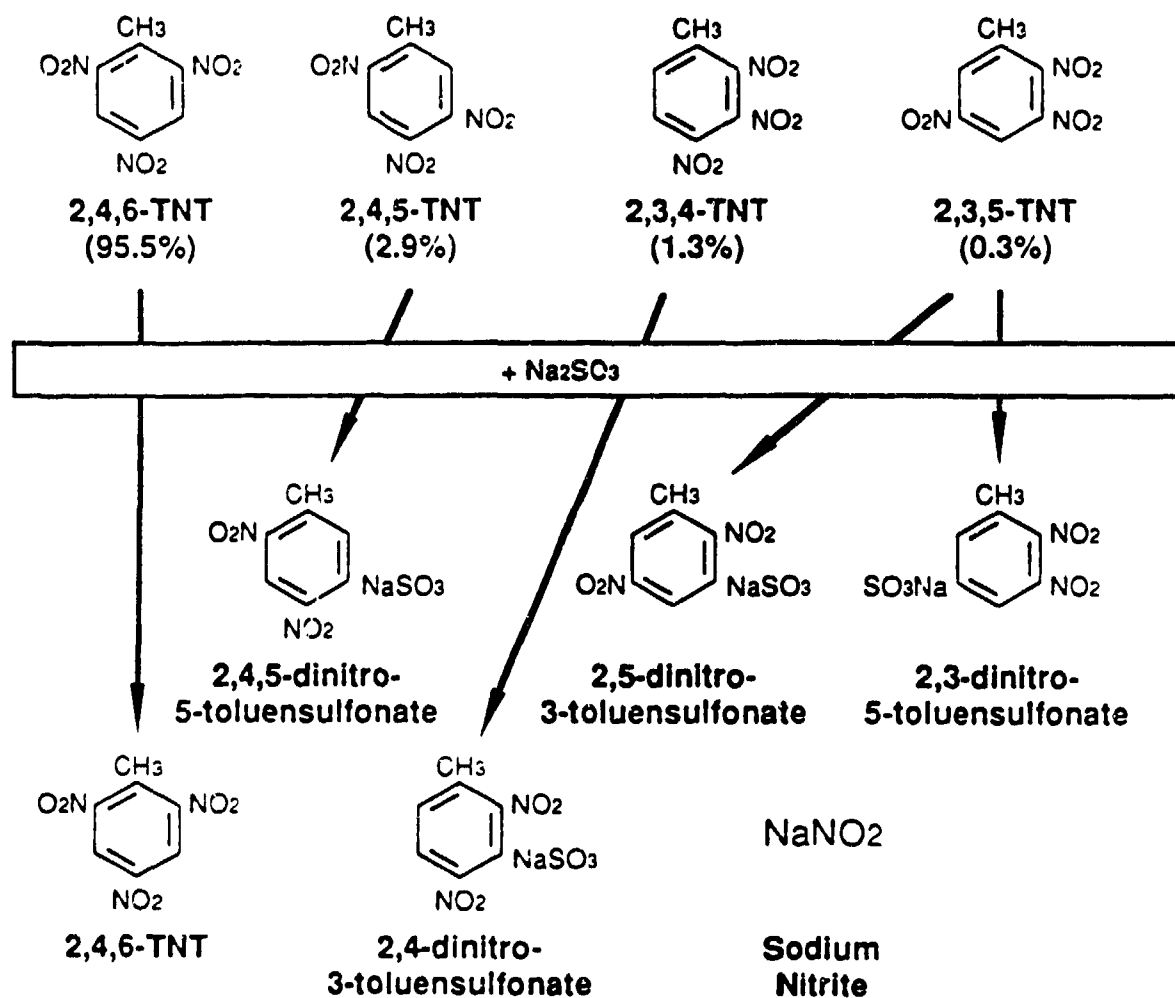


Figure 1-2. TNT purification with sodium sulfite.

Source: Technical Manual for Military Explosives
TM-9-1300-214, Undated.

process yields TNT that satisfies specifications. Figure 1-2 is a schematic of the TNT purification process. This solution of sodium dinitrotoluene sulfonates and trace amounts of other organic compounds are principal components of the TNT production wastewater or red water.

A recurring and fallacious assumption is that red water is a concentrated form of pink water. This assumption has led to erroneous conclusions that pink water treatment technologies can readily be adapted to red water treatment with only minor modifications. This is not the case.

Pink water is the resultant wastewater from wash down during LAP operations and consists primarily as an aqueous TNT solution in which the TNT concentration is in the 100-ppm range. Other components of pink water include cyclotrimethene trinitramine (RDX), cyclotrimethelene tetranitramine (HMX), and wax. The concentration of ionic compounds in pink water is zero or very low. Conversely, RAAP red water is about 15 percent dissolved solids (150,000 ppm), of which roughly 7 percent comprises inorganic salts (sodium sulfite, sodium sulfate, sodium nitrite, and sodium nitrate) and roughly 8 percent comprises sodium salts of dinitrotoluene sulfonic acids. Covalent organic compounds such as TNT are present in only trace amounts. Dinitrotoluene sulfonic acids are strong organic acids, and conversion of the organic anions to unionized acids requires a pH of 1 or less. This precludes or, at best, severely restricts the use of technologies that treat only unionized organic compounds (e.g., carbon adsorption) or that separate organic and inorganic compounds (e.g., foam fraction and solvent extraction). Also, because of the high concentrations and wide variety of dissolved solids involved, some of the chemical species will probably absorb energy (e.g., ultraviolet light and ultrasonic energy). This may preclude the use of such methods for red water even though they have been successful for pink water. Reduced inorganic anions such as sulfite and nitrite in red water are oxidizable and would react with chemical oxidizing agents such as ozone, hydrogen peroxide, and calcium hypochlorite that might be used to oxidize organic matter. This would render chemical oxidation both more difficult and more expensive.

SECTION 2

PRELIMINARY EVALUATION OF WASTEWATER DISPOSAL PROCESSES

The objective of this study was a technical investigation of the technologies available or potentially feasible for the treatment and/or abatement of red water generated during TNT purification at Army ammunition plants. This section presents the results of the preliminary screening of the 30 technologies. The use of a decision tree in the preliminary evaluation gave the technologies the benefit of doubt and recommended them for second stage evaluation unless some definitive reasons existed for their elimination.

2.1 TECHNICAL APPROACH

Seventeen technologies were originally proposed for evaluation by USATAHMA. These technologies included 10 processes that were investigated in the 1980 CSL report. In this report, CSL ranked the treatment methods based on a set of criteria that included environmental effectiveness, cost, and status of development. Seven other technologies were proposed by USATHAMA as potential candidates for red water treatment. Other treatment technologies with the potential of abating red water pollution were added to the list during the course of this investigation. Table 2-1 lists all the technologies evaluated and groups them according to the basis for their inclusion.

The purpose of the preliminary screening process was to evaluate numerous technologies initially, but to aim a more extensive evaluation only at those technologies offering potential for red water treatment. This method precluded overlooking any potentially promising technology while ensuring that extensive effort would not be wasted on technologies showing little promise for red water treatment. This "Go/No-Go" procedure divided the technologies into two groups: those that would receive further evaluation and those eliminated from further consideration.

TABLE 2-1. TECHNOLOGIES SELECTED FOR PRELIMINARY SCREENING

Technologies Listed in the CSI Report

Sonoco Sellite Recovery Process
Magnesium Sulfite Purification
Nitric Acid Purification
Fluidized Bed Reduction
Concentration followed by Incineration and Landfill
Tampella Recovery Process
Ammonium Sulfite Purification
SCA Billerud Recovery
Reverse Osmosis
Acidification

Additional Processes Proposed by USATHAMA

Argonne National Laboratory Process
Biodegradation by White Rot Fungus in a Packed Bed Reactor
Biodegradation by British Royal Ordnance
Hybrid Thermal Treatment System (HTTS)
Slagging Rotary Kiln
Submerged Combustion
Supercritical Water Oxidation

Additional Technologies

Biodegradation by White Rot Fungus in a Rotating Biological
 Contactor
Carbon Adsorption
Catalyzed Wet Oxidation
Composting
Freeze Technology
Ion Exchange
Land Treatment
Liquid-Phase Oxidation (Ozone, Hypochlorite, or Peroxide
 with Ultrasound or U.V.)
Plasma Arc
Solidification/Stabilization
Surfactant Technology
Thermal Separation
Wet Air Oxidation

In the preliminary screening process, the 1980 CSL report was used as a baseline for evaluation. Technologies that were not selected for evaluation in the report and have not since been further developed were eliminated from the evaluation process to avoid expending needless effort on technologies previously judged unworthy of further evaluation.

Several sources of information were used to evaluate the 30 technologies. Literature searches were conducted by PEI and USATHAMA to identify research pertaining to TNT purification and red water treatment and disposal. Literature published after 1980 was of particular interest for the 10 technologies evaluated in the 1980 CSL report. A listing of the literature data bases used in the literature search for information on TNT red water and treatment is provided in Table 2-2. Vendors and researchers were contacted to ascertain the developmental status of various processes and their potential for successfully treating red water. Mr. James Carrazza of ARDEC was especially helpful in sharing his experience with several of the technologies evaluated.

TABLE 2-2. DATA BASES INVESTIGATED BY USATHAMA AND PEI IN LITERATURE SEARCH FOR INFORMATION ON TNT RED WATER AND ITS TREATMENT^a

Agricola (1979-1988)	Environmental Bibliography
Chemical Business Newbase	Federal Index
Chemical Engineering Abstract	Federal Register Abstract
Chemical Exposure	GPO Monthly Catalog
Chemical Industry Notes	Heilbrow
Compendex Plus (1970-1988)	NTIS (1980-1988)
Current Technology Index	Paperchem (1967-1988)
DMS Defense Newsletter	Pollution Abstracts
DTIC	Scisearch
Enviroline (1970-1988)	Water Resources Abstract (1968-1988)

^a Time periods of search are indicated in parentheses when known.

Also, Foster Wheeler stated in a February 10, 1988, report entitled "Investigations Into the Status of Possible Alternatives for Disposal and/or Reuse of TNT Red Water" that literature searches in the following data bases provided no information pertinent to TNT red water:

- Chemical Abstracts (1958-Present)
- DOE Energy Department Files (1974-Present)
- Dissertation Abstracts (1961-Present)
- Applied Science & Technology Index (1958-Present)

2.2 PRESCREENING DECISION TREE

In the preliminary screening of potential red water treatment/abatement technologies, a "prescreening decision tree" was developed. The decision tree contained a series of questions requiring yes or no answers and branches to other questions, depending on the responses. A disqualifying answer to any critical questions resulted in the elimination of the technology from further consideration. Figure 2-1 presents a visual display of the tree created to show the logic behind the evaluations.

A brief discussion of each of the questions included in the prescreening decision tree is provided here.

- Is the technology compatible with red water? This question serves to identify and eliminate those processes whose operating parameters are not consistent with the characteristics of the red water waste stream.
- Was the technology evaluated in the 1980 Chemical Systems Laboratory (CSL) Report? In 1980, CSL prepared a report that evaluated 10 technologies in detail, selected three technologies as having the greatest red water treatment potential, and recommended the implementation of one technology. The general consensus among USATHAMA, ARDEC, and the Production Base Modernization Activity (PBMA) is that information presented in the CSL report was useful and correct as of 1980. This report thus served as a baseline of information for the 10 technologies evaluated. This branch in the decision tree provided for quick elimination of technologies that were evaluated in 1980, received low ratings, and have not been further developed since.
- Was the technology recommended for further evaluation in the 1980 CSL report? Those technologies selected in 1980 as having potential for red water treatment were again considered for further evaluation. Those technologies not recommended in the 1980 CSL report were possibly considered further. After this branch in the decision tree, technologies that were recommended for further evaluation in 1980 were subjected to the same questions as technologies not previously considered.
- Have positive developments been made with the technology since 1980? Because the 1980 CSL report was used as a baseline, those technologies that were ruled out in 1980 and have not been developed further were most likely not worthy of further evaluation. Those technologies that have been developed somewhat since the 1980 CSL report were possibly considered for further evaluation.
- Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? Technologies that were not

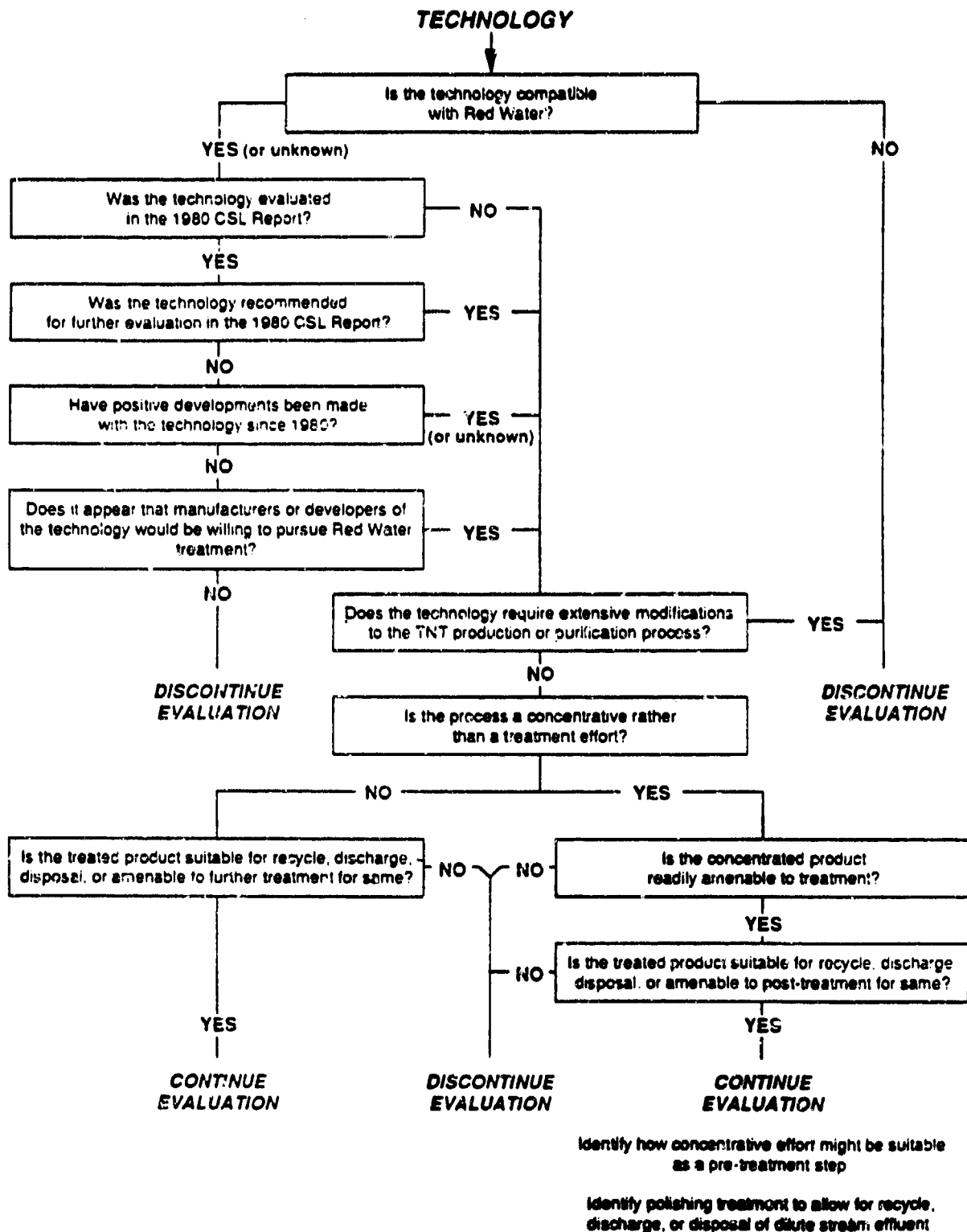


Figure 2-1. Prescreening decision tree.

recommended in the 1980 CSL report, have not had further developments, and are of no interest to developers of the technology were discontinued from evaluation. Those technologies for which the developer indicated interest, but have not been developed since 1980, possibly remained in consideration.

- ° Does the technology require extensive modifications to the TNT production and purification process? The Canadian Industries Limited (CIL) TNT production and purification processes have been implemented in U.S. TNT production facilities. USATHAMA, ARDEC, and PBMA have indicated that technologies requiring extensive modifications to these processes will not be allowed since the ramifications may affect TNT performance and have a major cost impact if existing facilities must be extensively modified.
- ° Is the process a concentrative rather than a treatment effort? This question separated the technologies that treat red water from those that only concentrate red water.
- ° Is the concentrated product readily amendable to treatment? Concentration technologies that are capable of producing a concentrated stream readily amenable to further treatment and an effluent suitable for recycle, discharge, disposal or post-treatment for the same were considered as a potential pre- and/or post-treatment mechanism.
- ° Is the treated product suitable for recycle, discharge, or disposal or amenable to further treatment for same? Technologies that reached and passed this question on the treatment or concentration side were possibly suitable for treating red water and producing environmentally acceptable products, including any resulting effluent and byproducts.

2.3 RESULTS OF PRELIMINARY SCREENING

As a result of the application of the decision tree to the original 30 technologies chosen for evaluation, 15 were eliminated from further consideration and 15 were selected for further evaluation. Table 2-3 presents those technologies that survived the preliminary screening process, and Table 2-4 presents those technologies that did not. The technologies have been divided into biological treatment processes, chemical/physical treatment processes, thermal treatment processes, processes for elimination of red water production, and mixed/other processes.

Of the 10 technologies evaluated in the 1980 CSL report, only the Sonoco Sellite Recovery Process survived the preliminary screening process. Most of

TABLE 2-3. TECHNOLOGIES SELECTED FOR FURTHER EVALUATION^a

Biological Treatment Processes

Biodegradation by British Royal Ordnance^b
Biodegradation by White Rot Fungus in a Rotating Biological Contactor^c
Biodegradation by White Rot Fungus in a Packed-Bed Reactor

Chemical/Physical Treatment Processes

Catalyzed Wet Oxidation
Liquid-Phase Oxidation (Ozone, Hypochlorite, or Peroxide with Ultrasound or U.V.)
Surfactant Technology
Wet-Air Oxidation

Thermal Treatment Processes

Hybrid Thermal Treatment System (HTTS)
Plasma Arc
Slagging Rotary Kiln
Submerged Combustion
Supercritical Water Oxidation
Thermal Separation

Processes for Elimination of Red Water Production

(None)

Mixed/Other Treatment Processes

Argonne National Laboratory Process
Sonoco Sellite Recovery Process

^a Initially, 16 technologies survived the preliminary screening. Three technologies were dropped during the secondary evaluation (see footnotes b, c and d). One technology (circulating-bed combustion) was identified following the preliminary screening and was added to the list for secondary evaluation. Thus, a total of 14 technologies were evaluated in the secondary evaluation.

^b Biodegradation by British Royal Ordnance survived the preliminary screening because of a lack of available data. No additional information could be obtained during the secondary evaluation, so the process was not considered further.

^c Developers of the Biodegradation by White Rot Fungus on a Rotating Biological Contactor conceded that Biodegradation by White Rot Fungus in a Packed Bed Reactor was superior. Thus, Biodegradation by White Rot Fungus on a Rotating Biological Contactor was not considered in the secondary evaluation.

^d Licensing of an existing industrial technology and shipment of red water to the facility for treatment/disposal were considered short-term rather than long-term options, and thus were removed from further consideration by USATHAMA. Since that time, PMBA has submitted a CIL red water sample to duPont for treatment evaluation. At the time of finalizing this report, evaluation results were not yet available.

TABLE 2-4. TECHNOLOGIES ELIMINATED FROM FURTHER EVALUATION

Biological Treatment Processes

Composting
Land Treatment

Chemical/Physical Treatment Processes

Acidification
Carbon Adsorption
Freeze Technology
Ion Exchange
Reverse Osmosis
Solidification/Stabilization

Thermal Treatment Processes

Fluidized-Bed Reduction
Incineration by CIL
SCA Billerud Recovery
Tampella Recovery Process

Processes for Elimination of Red Water Production

Ammonium Sulfite Purification
Magnesium Sulfite Purification
Nitric Acid Purification

Mixed/Other Treatment Processes

(None)

the technologies evaluated herein were eliminated because they were not recommended in the 1980 CSL report and have not undergone any positive developments since that time.

Nitric acid purification and magnesium sulfite purification were selected for further consideration in the preliminary evaluation stage of the 1980 CSL report. These technologies have been eliminated from further evaluation in this project because they involve changing the TNT purification process, which USATHAMA, ARDEC, and PBMA have indicated is undesirable. These technologies show promise, however, as a solution to the red water environmental problem; emphasis is on changing the characteristics of the wastewater rather than on treating red water. If the respective agencies change their current position on using the Canadian Industries Limited (CIL) sellite

purification process, nitric acid purification and magnesium sulfite purification should be evaluated further as red water abatement technologies.

The preliminary evaluations are provided in Appendix C. Each evaluation includes a description of the technology, a discussion of factors relevant to whether the technology should be evaluated further, a discussion of the steps in the prescreening decision tree, and a diagram of the prescreening decision tree showing the path that each particular technology followed.

SECTION 3

DETAILED EVALUATION OF WASTEWATER DISPOSAL PROCESSES

This section presents the results of the secondary evaluation of the technologies that survived the preliminary screening. The technologies are compared on the basis of technical considerations for identification of those most worthy of pilot-plant testing and further evaluation.

The purpose of this investigation was to consolidate, under one cover, the information regarding numerous technologies for the treatment of red water. The detailed technical discussions and calculations provided herein have been collected from other sources. PEI was not, and is not, in a position to challenge the validity of the data provided in the literature. Thus, it was assumed that the available information was correct within reasonable tolerances and that verbal and unpublished communications were accurate. PEI was not provided red water to perform any of its own investigations or data certification. Only the conclusions drawn from the information obtained and the recommendations indicated are direct results of this technology investigation.

This report successfully satisfies the objectives in that:

1. Considerable information regarding a large number of technologies for red water treatment is presented herein.
2. A subjective, yet consistent evaluation of all of the technologies evaluated was performed to provide a set of recommendations for follow-up work.

3.1 TECHNICAL APPROACH

Fifteen technologies survived the first round of evaluations. Circulating bed combustion, a proprietary thermal treatment technology marketed by Ogden Environmental Services, was discovered after the preliminary screening and was added to the list. No additional information was obtained on biodegradation by the British Royal Ordnance Technology, so this technology was dropped.

Biodegradation by white rot fungus on a packed bed was found to have advantages over biodegradation by white rot fungus on a rotating biological contactor, so only the packed bed option was evaluated. Thus, only the 15 wastewater treatment/disposal processes listed in Table 3-1 received detailed evaluation.

TABLE 3-1. WASTEWATER DISPOSAL PROCESSES
RECEIVING DETAILED EVALUATION

Biodegradation by white rot fungus on a packed-bed reactor
Catalyzed wet oxidation
Liquid-phase oxidation
Solids precipitation with surfactant
Wet-air oxidation
Hybrid thermal treatment system
Plasma arc
Slagging rotary kiln
Submerged combustion
Supercritical water oxidation
Thermal separation
Argonne National Laboratories process
Licensing existing industrial technology
Sonoco Sellite Recovery Process
Circulating-bed combustion

3.1.1 Evaluation Procedures

The objective of the evaluation procedures was to obtain relevant and comparative rankings of the wastewater treatment processes to identify candidate processes for pilot-plant testing and further evaluation. PEI and USATHAMA derived a weighted scale for the process evaluation. Factors and their weightings are as follows:

- ° Theoretical potential of the technology for suitable treatment of red water--10 points maximum.
- ° Current application and status of the technology--20 points maximum. A technology successfully demonstrated on RAAP red water would receive the maximum award (there is no such technology); a treatment based on only theoretical or paper studies would receive a much lower rating.
- ° Environmental impact--50 points maximum. This award takes into account air emissions, water emissions, solid wastes generated, and awards credit for producing a recyclable product.

- ° Time and cost to develop to the implementation stage--10 points maximum. This award recognizes the time and cost required to develop the technology from its present stage to an implementable technology. The award does not take into account capital and annual costs because some of the technologies are not sufficiently developed to allow reliable capital and annual cost estimates.
- ° Complexity of process, system operation, and flexibility of operating parameters--20 points maximum. This award recognizes that the more complex and less flexible the process, the more difficult it will be to develop, operate, and control the final installed, in-plant system satisfactorily. The less complex the system is, the higher the award.

Table 3-2 presents the evaluation criteria and the bases for making partial awards. The highest possible total award is 110 points. A zero rating on a key point (e.g., theoretical potential) or for an irresolvable air or water environmental problem would only reduce the rating by 10 points out of 110 and would not necessarily eliminate the technology on a comparative ranking basis. Nevertheless, such an irresolvable obstacle would eliminate the technology on a practical basis. Such technologies should have been eliminated during the preliminary evaluations.

Of the 14 detailed evaluations, 8 were prepared by Hunter/ESE Environmental Services, Plymouth Meeting, Pennsylvania (Michael E. Resch, P.E., Project Manager) in coordination with the Hunter/ESE Gainesville, Florida, office; and 6 were prepared by PEI Associates, Inc., Cincinnati, Ohio, and Arlington, Texas (John A. Wentz, Project Manager; John E. Spessard, Ph.D., P.E.; William E. Gallagher, P.E.; and Roxanne B. Sukol).

The Hunter/ESE evaluations provided detailed discussions of the pertinent factors, sometimes without making point awards. Ms. Sukol's evaluation also included detailed discussions with point awards made by Dr. Daniel Sicu of Combustion Engineering Environmental, Inc., and Dr. Thomas Joyce of the North Carolina State College of Forest Resources. Dr. Sicu's and Dr. Joyce's point awards were not in agreement. Dr. Spessard and Mr. Gallagher made point awards on the technologies they evaluated.

To assure consistency among all the evaluated technologies, PEI has prepared the point awards for all the technologies appearing in this section for better internal consistency. Objectives were as follows:

TABLE 3-2. SECONDARY-LEVEL EVALUATION CRITERIA FOR
RED WATER TREATMENT TECHNOLOGY EVALUATION

Evaluation criteria	Maximum point value					
1. Theoretical potential of the technology for suitable treatment of red water (R.W.). (Points are not deducted at this stage because of limited or no field experience.)	10					
Unlikely theoretical potential	0 - 2					
Low theoretical potential	3 - 5					
High theoretical potential	6 - 8					
Extremely high theoretical potential	9 - 10					
2. Current application and status of technology. (Points assigned by identifying the most successful application.)	20					
	Waste Stream Similiarity to R.W.					
	Solid		Liquid		R.W. from another AAP	RAAP R.W.
	Not Simi- lar	Simi- lar	Not Simi- lar	Simi- lar		
Process demonstrated at the laboratory or pilot plant scale.	12	14	13	16	18	20
Sufficient portions of process demonstrated at the laboratory or pilot plant scale.	10	12	11	14	14	16
Small portion of process demonstrated at the laboratory or pilot-plant scale.	4	6	5	8	10	12
Theoretical or paper studies provide basis for predicting emissions.	1	3	2	5	6	8

(continued)

TABLE 3-2 (continued)

Evaluation criteria	Maximum point value
<p>3. Environmental impact. 50 (Range of score based on degree of certainty and ease of compliance. If no emissions are generated in a given category all possible points of that category are awarded.)</p> <p>Wastewater discharge regulations 0 - 10 Air emission regulations 0 - 10 Solid hazardous waste requiring landfilling 0 - 20 Recyclable material 0 - 10 (points credited for recyclable material)</p>	
<p>4. Time and cost to develop to 10 implementation stage.</p> <p>Process development time:</p> <p>< 1 year 5 1 - 3 years 3 - 4 3 - 5 years 2 - 3 > 5 years 1 - 2</p> <p>Process development cost:</p> <p><\$500,000 5 \$500,000 - \$750,000 3 - 4 \$750,000 - \$1,000,000 2 - 3 >\$1,000,000 1 - 2</p>	
<p>5. Complexity of process, system 20 operation, and flexibility of operating parameters.</p> <p>Process complexity 0 - 5 Difficulty of operation 0 - 5 Flexibility of operating parameters 0 - 5 Miscellaneous (evaluator judgment of technology) 0 - 5</p>	
Total maximum number of points	110

- ° To provide meaningful and consistent awards.
- ° To make the awards on the basis of the technical evaluations and to be consistent with the conclusions provided by the evaluations.

3.1.2 Technology Evaluation Criteria

Theoretical Potential of the Process--

The full 10 points were awarded for theoretical potential unless there were specific reasons to believe that the technology was infeasible. Deductions were modest if the problems appeared to be resolvable.

Current Application and Status of Technology--

The criteria used are those set forth in Table 3-2. The maximum possible award of 20 points has not been made because RAAP red water was not used in any of the tests. Some reductions from preliminary evaluation awards were made to reflect that red water differs from pink water. Awards are higher for well-developed technologies that have successfully treated a variety of wastes and in cases where existing equipment is available to permit pilot-plant testing.

Environmental Impact--

Only the Sonoco Seilite Recovery Process and Catalyzed Wet Oxidation Process were given any credit for recyclability. Less than the full 10 points were awarded to SSRP because of the unresolved issue that the buildup of dissolved metals and other impurities will result in a bleed stream that may require treatment prior to disposal. Minimal credits were awarded CWO for recyclability because the recyclable product was the added catalyst with unknown reusability after recovery.

Environmental emission awards were reduced when the treatment process appeared likely to generate a stream requiring additional treatment. Awards were also reduced when the technology was not well enough defined for estimation of resulting emissions and determination of needed additional emission controls. Wastewater discharge awards were reduced when incomplete destruction of red water organic compounds left remaining uncharacterized and potentially toxic organic compounds.

Time and Cost to Develop to Implementation Stage--

Because an acceptable process for treating red water is a prerequisite for the startup of a TNT plant, the time and cost required to implement a technology are pertinent factors weighted at 5 points each. (Capital cost and annual operation and maintenance costs would be important considerations but these can only be addressed following completion of recommended bench and pilot testing.) Depending on the current state of development of the technologies, some estimates of the cost and time required represent rough approximations.

Complexity of Process--

The ideal process would be a single stage one operating at ambient temperature and pressure and generating no corrosive, ablative, or toxic products, wastes, or emissions. It would operate in an automated mode, require minimal operator attention, and be able to handle wide variations in feed rate, feed composition, and operating parameters. It would be easy to start up and shut down. Enough units would be in commercial service to provide thousands of hours of operating experience that could assist in development of the process for red water treatment. Such a technology would receive the full 20 points.

Process complexity accounts for a possible 5 points. Deductions are made for multiple processing steps and operation at high temperature or high pressure, in a corrosive environment, and with solids circulating at high velocities (ablation). Any combination of these conditions tends to result in more frequent breakdowns. More attention to materials of construction and control of operating parameters become mandatory.

The difficulty of operation factor is also worth 5 points. A complex operation will require full operator attention, and an operator's error or lack of proper attention is likely to produce a process upset or system breakdown. [Also, each full-time operator working an 8-hour shift costs about \$41,600 per year (2080 hours/year x \$20/hour).]

Red water varies in both composition and rate of generation. A process that can handle fluctuations and surges is more reliable. This factor is worth 5 points.

The evaluator's judgment of the technology is worth 5 points. Factors considered include a higher allowance for a technology that is currently in commercial service and that is well enough defined to permit reasonable time and cost estimates to be made.

3.2 EVALUATION OF THE TECHNOLOGIES

A 110-point scale was established for the 14 technologies. Appendix D presents the Hunter/ESE and PEI Associates, Inc. evaluations of the technologies, which serve as the bases of these evaluations. The assigned point values for each constraint for each technology are summarized in a weighted matrix form in Table 3-3 at the end of this section. Detailed discussions of the evaluations are presented in Appendix D, and the sources of information are referenced therein.

3.2.1 Biodegradation by White Rot Fungus on a Packed-Bed Reactor

Theoretical Potential of the Process--

The assigned theoretical potential is 8 of 10. Deductions were made because 1) the technology does not always provide 100 percent destruction of organic matter and could produce a waste stream requiring additional treatment by yet-to-be-developed technology, and 2) the effectiveness of the white rot fungus in a high concentration ionic salt medium has not been established.

Current Application and Status of Technology--

Current application and status has been assigned 7 of the 20 points. Preliminary tests have been run on aqueous TNT solutions, which most closely resembles red water. No evidence was uncovered to indicate that this technique has ever been used on a solution containing 8 percent dissolved organic solids (as red water does).

Environmental Impact--

Environmental impact awards are assigned 10 points for air emissions, 3 for water emissions, and 4 for solid/hazardous waste. The treatment takes place in a packed bed at ambient temperatures. Air emissions may or may not be a factor; however, volatile organic compounds (VOCs) could be intermediate products and a possible source of air emissions. Biological degradation of

red water organics may be incomplete because of the relatively high dissolved organic salt concentration and the high ionic strength of the solution. Red water has a dissolved organic salt concentration of approximately 80,000 ppm, and 99.9 percent destruction of organic matter would still produce a stream containing approximately 80 ppm dissolved organics (about the concentration of pink water). This technology could quite possibly produce a water stream requiring subsequent treatment by a yet-to-be-developed technology.

Solid waste is rated at 4 of 20 points. Contaminated bed packing would have to be disposed of as hazardous waste unless it were eligible for delisting. Finely divided and contaminated bed packing produced by attrition could be in the effluent stream. This material might have to be collected and treated as hazardous waste.

Time and Cost to Develop to Implementation Stage--

Time and cost to reach implementation were each assigned 3 of a possible 5 points. The technology is undeveloped, and an informed estimate is not possible; however, the simplicity and straightforwardness of the process justifies the rating.

Complexity of Process--

Assigned ratings are 3 of 5 points for process complexity, 4 of 5 for difficulty of operation, 3 of 5 for flexibility of operating parameters, and 3 of 5 for evaluator judgment of the technology. The process is inherently simple, and higher ratings would be appropriate except for the possibility of effluent treatment.

3.2.2 Catalyzed Wet Oxidation

Theoretical Potential of the Process--

The assigned theoretical potential is rated as 4 of 10 points. Deductions were made because 1) not all of the starting organic compounds are destroyed, 2) the majority of the original organic carbon is present in the form of uncharacterized organic compounds that may be classified as hazardous, and 3) the process is most efficient at a pH of 4 or less. Red water acidification as part of a desulfonation research project resulted in violent explosions due to the production of diazonium salts. Acidification

also resulted in the production of an unstable precipitate that would be an extremely hazardous waste.

Current Application and Status of Technology--

Current application and status have been assigned 7 of 20 points. The technology has been used on a slurry containing 23 percent TNT. It has not been used on solutions containing high concentrations of ionic organic compounds similar to red water.

Environmental Impact--

Assigned points for environmental impact are 4 for air emissions, 2 for water emissions, and 17 for solid/hazardous waste requiring disposal. Organic compounds are changed from the original compounds to different yet-to-be-characterized compounds. The air impact point assignment is low because of 1) hydrogen bromide emissions from a hot acidified solution; and 2) the probability of generating VOC emissions. The aqueous effluent will contain organic compounds and will require additional treatment by some yet-to-be defined process. Also, solids may be produced that require subsequent treatment and/or disposal as hazardous waste. The potential exists for recovery of hydrogen bromide and sulfuric and nitric acids through expensive electromembrane technology and acid recovery. Recyclability for the CWO process received 2 of 10 recyclability points.

Time and Cost to Develop to Implementation Stage--

Catalyzed wet oxidation will be carried out at a yet-to-be-determined temperature and pressure. The effluent streams, VOC emissions, and any precipitates will have to be treated by a yet-to-be-developed technology. Prospects are for a potentially lengthy and expensive research and development effort. Point assignments are 3 of 5 for time and 3 of 5 for cost.

Complexity of Process--

The catalyzed wet oxidation part of the technology is only moderately complex. Nevertheless, deductions are appropriate to reflect the need for additional treatment of air, water, and solid effluents by yet-to-be developed technologies. Point assignments are 2 for process complexity, 1 for

difficulty of operation (the operation is potentially hazardous), 2 for flexibility of operating parameters (because of the potential hazard), and 1 for the evaluator's judgment of the technology.

3.2.3 Liquid-Phase Oxidation

Theoretical Potential of the Process--

Liquid phase oxidation is assigned a theoretical potential of 6 of 10 points because organic compounds are converted to other organic compounds instead of being completely converted to carbon dioxide and water. These oxidation product organic compounds may require additional treatment by a yet-to-be developed technology.

Current Application and Status of Technology--

Liquid phase oxidation has achieved partial oxidation of pink water solutions. Oxidation was complete enough to remove the pink color, but uncharacterized organic compounds remained. The fact that oxidation requires large excesses of chemical oxidants renders the technology economically unacceptable. The current application rating is 7 of 20 points.

Environmental Impact--

Environmental impact awards are 7 points for air emissions, 3 for water emissions, and 17 for solid waste. The deduction for compliance with air emissions is due to 1) no testing with either red water or a similar concentrated solution, 2) possible VOC emissions of uncharacterized organic compounds, and 3) possible undesirable emissions (e.g., chlorine and ozone) from excess oxidants. The water award is low because 1) uncharacterized organic compounds are in the waste stream, and 2) possible unreacted oxidant in the waste stream may require treatment. The solid waste deduction is due to the possibility that precipitates from oxidation may require treatment.

Time and Cost to Develop to Implementation Stage--

This technology probably would require a lengthy and expensive development program. The assigned ratings are 2 of 5 points each for time and cost. Process parameters to be established include the following:

- ° Selection of the proper oxidant.

- ° Optimum process conditions (temperature, pH, etc.).
- ° Characterization of organic compounds produced by oxidation.
- ° Treatment technologies for these organic compounds.

Complexity of Process--

Inherently, liquid phase oxidation should be a simple process. Deductions are made because of the undefined process parameters and the possibility of generating waste streams that require treatment. Assigned values are 2 of 5 points for process complexity, 3 of 5 for difficulty of operation, and 3 of 5 for flexibility of operating parameters. Evaluator's judgment was 1 of 5 points because all experimental work indicates that large excesses of oxidant will be required at a high cost.

3.2.4 Solids Precipitation With Surfactant

Theoretical Potential of the Process--

The theoretical potential rating is 7 of 10 points. The deduction is due to the prior development work being with neutral organic molecules such as TNT rather than with dinitrotoluene sulfonate anions such as would be encountered with red water. The salt of a large cation (such as a quaternary amine) and a large anion (such as a dinitrotoluene sulfonate) probably would be insoluble, however, and precipitation should be feasible. Nevertheless, the liquor would require further treatment to remove unprecipitated red water anions and excess surfactants.

Current Application and Status of Technology--

Brooklyn Polytechnic Institute performed preliminary experiments with red water. In a personal communication, James Carrazza of the U.S. Army Research and Development Laboratory indicated that 1) a clear effluent was not obtained, 2) the quaternary ammonium surfactant used as a precipitator is in itself toxic, and 3) the issue of VOC emissions and potential toxic compounds in the ash from possible incineration of the precipitate had not been addressed. The point award is 7 of 20.

Environmental Impact--

Solids precipitation with surfactants presents major unresolved environmental problems. Treatment may increase rather than solve environmental

problems. Point awards are 6 of 10 for air emissions, 0 of 10 for water emissions, and 0 of 20 for solid/hazardous waste. Commercial-quality quaternary amines are contaminated with malodorous and possibly toxic impurities that are potential VOC emissions. The wastewater would contain excess quaternary amines (to ensure complete precipitation) and possibly unprecipitated red water constituents. These wastewater streams would require additional treatment.

The precipitated salt of the quaternary amine cation and the dinitrotoluene sulfonate anion would present a particular problem, as both the anion and cation would be toxic. The filtered solid precipitate would be appreciably less than 100 percent solids by weight with entrained liquor. The liquor would contain dissolved red water solids and require additional treatment.

Time and Cost to Develop to Implementation Stage--

Surfactant precipitation technology has serious problems that may not be solvable. Point awards are 2 of 5 each for time and cost.

Complexity of Process--

Although precipitation is a simple process, the technology for treating both the precipitate and the mother liquor may be more complex and is completely undefined. Awards are 1 of 5 points for process complexity, difficulty of operation, and flexibility of operating parameters, and 0 of 5 for the evaluator's judgment. Aside from the unresolved technical problems and assuming quantitative precipitation, the quaternary amine cost would be 69 cents per gallon of red water, which is prohibitively expensive.

3.2.5 Wet Air Oxidation

Theoretical Potential of the Process--

In 1956, Zimpro Corporation (now Zimpro/Passavant Corporation) performed laboratory-scale investigations using red water from the Joliet Army Ammunition Plant and the Volunteer Ordnance Works. The chemical oxygen demand was reduced from 65.2 g/L to 0.9 g/L, a 97.1 percent reduction. If the oxidized liquid can be delisted as a hazardous waste and is treatable in a standard wastewater treatment technology, the rating for theoretical potential is 9 of 10 points. (If the liquid cannot be delisted, the rating would be 4 of 10 points.)

Current Application and Status of Technology--

Wet air oxidation was successfully used on red water from two U.S. Army facilities other than Radford. Because the issue of delisting and treatment of the effluent has not been addressed, however, the point award was reduced from 18 of 20 to 14 of 20.

Environmental Impact--

Wet air oxidation occurs in a closed system at elevated temperature and pressure. Air emissions are possible when the reactor is depressurized; however, these emissions should be controllable. The air emission rating is 9 of 10 points. The question of delisting and treating the wastewater has not been addressed; therefore, the wastewater discharge rating is 5 of 10 points. The only solid resulting from the previous red water oxidation was ferric oxide; however, because RAAP red water was not used in the test, the point rating was reduced to 16 of 20.

Time and Cost to Develop to Implementation Stage--

Zimpro/Passavant Corporation has existing pilot plant equipment available for testing, which would reduce the time required for process development. Ratings are 4 of 5 points for time and 3 of 5 for cost. Treatment requirements for the effluent is an unresolved issue that has an impact on both time and cost.

Complexity of Process--

Wet air oxidation takes place in a pressurized vessel. Representative conditions are pressures between 2,069 and 20,690 kilopascals (300 to 3000 psig) and temperatures between 174° and 327°C (347° to 621°F). This indicates a complex process requiring attention for control of the operating parameters, but one with reasonable flexibility. Point ratings are 2 of 5 for process complexity, 3 of 5 for difficulty of operation, and 3 of 5 for operating flexibility. Wet air oxidation has been tested on red water, and laboratory-scale results are promising. The evaluator's judgment award is 5 of 5 points.

3.2.6 Hybrid Thermal Treatment System

Theoretical Potential of the Process--

The hybrid thermal treatment system (HTTS) is a two-stage incineration process. The first stage is a rotary kiln, and the second stage is an

incinerator. This technology is well established and in commercial operation. The theoretical potential is rated as 8 of 10 points.

Current Application and Status of Technology--

This technology has been demonstrated on explosives-contaminated soil at the Corn Husker Army Ammunition Plant. The TNT and RDX removal efficiencies were 99.99 percent. The rating is 16 points of a possible 20 because although the system is currently operating at full-scale, the only demonstrations has been with solids.

Environmental Impact--

Red water evaporation and incineration are potential sources of air emissions, contaminated wastewater (due to spraying and mechanical losses), and contaminated ash. All of these potential problems are probably resolvable, but they have not been addressed. Process development work will be required. Ratings are 5 of 10 points each for air and water emissions and 7 of 20 for solid waste. Water emissions might be avoided by using an evaporator rather than a rotary kiln.

Time and Cost to Develop to Implementation Stage--

Because the equipment already exists, the development time and cost would be less; however, processing conditions and auxiliary equipment might have to be modified to convert from processing a solid to processing a liquid. The time and cost ratings are 4 of 5 points each.

Complexity of Process--

Red water is essentially a 15 percent aqueous solution of organic and inorganic sodium salts. Appendix E presents a memorandum detailing interviews with incinerator and refractory vendors in which the effects of sodium salts on refractories are discussed. Findings indicate that the presence of sodium salts will make kiln and incinerator operation much more difficult and will increase capital and operation and maintenance costs. This problem will have an impact on all red water incineration treatment processes.

The process evaluation (see Appendix D) points out the following: 1) the nitrogen oxide reduction step is unproven, 2) the process may produce low-melting slag eutectics and submicron-sized particulates, 3) most of the ash will be water-soluble and cannot be landfilled, and 4) the process is

complex and requires control of relatively inflexible operating parameters. Ratings are 2 of 5 points each for process complexity, difficulty of operation, and flexibility of operating parameters; and 2 of 5 points for the evaluator's judgement of technology.

3.2.7 Plasma Arc

Theoretical Potential of the Process--

The plasma arc has been successfully used to treat hazardous wastes. Some of the problems associated with processing a waste with a high water content can be avoided by preliminary evaporation of most of the water. The theoretical potential rating is 5 of 10 points because red water is approximately 85 percent water.

Current Application and Status of Technology--

The SKF Plasma Technologies process is designed for the processing of pulp and paper industry black liquor and is used for that purpose. Black liquor is an aqueous solution containing dissolved sodium salts and organic matter similar to red water. The black liquor's fuel value, however, is much greater than that of red water. The plasma arc technology has not been used on red water. The current status of technology rating is 11 points of a possible 20.

Environmental Impact--

Environmental controls should be straightforward. A wet caustic scrubber will collect most of the acid gases, carbon particulates, and some NO_x . The scrubber wastewater will be the only liquid stream, and it should be treatable with existing technology. Emission controls will have to be fitted and designed for the plasma arc system. Ratings are 9 of 10 points each for air and water emissions and 17 of 20 points for solid waste.

Time and Cost to Develop to Implementation Stage--

The evaluator's estimate is 12 to 21 months and \$1,000,000. The time factor rating is 3 of 5 points and the cost factor rating is 2 of 5 points.

Complexity of Process--

Plasma arc processing requires plasma temperatures of acid gases and caustic solids, which will be demanding on refractories (see Appendix E) and

other materials of construction. Two full-time operators will be required, as will continuous analysis of the feed stream. With adequate control, some operating flexibility is possible. Process complexity and difficulty of operation are rated at 3 of 5 and 2 of 5 points respectively, flexibility of operating parameters is rated at 2 of 5 points, and the evaluator's judgment is rated at 1 of 5 points. The evaluator's judgment is influenced by the number of units necessary because of the limited throughput of each unit and by the treatment cost of \$1/pound, which is expensive even if most of the water is evaporated prior to processing.

Any available operating experience with pulp and paper industry black liquor would indicate process complexity, difficulty of operation, refractory operating life, and flexibility of operating parameters.

3.2.8 Slagging Rotary Kiln

Theoretical Potential of the Process--

Slagging rotary kilns are currently in active commercial use and have been used effectively on more than 10,000 types of wastes. Therefore, the theoretical potential rating is 9 of 10 points.

Current Application and Status of Technology--

Slagging rotary kilns have not been used on red water or a waste stream similar to red water. As with other incinerator technologies, prior evaporation of at least part of the water with a conventional evaporator could contribute to process efficiency. The SRK process has been demonstrated at full scale on other liquid wastes at various locations throughout Europe and the United States. The current application and status rating is 14 of a possible 20 points.

Environmental Impact--

Slagging rotary kiln technology is a potential source of air emissions, contaminated wastewater (due to spraying and mechanical losses), and contaminated ash. Although all of these problems are potentially solvable and have been addressed in other commercial applications of the technology, emission controls would have to be adapted to red water processing, and process development work would be necessary. Ratings are 6 of 10 points for air

emissions, 5 of 10 points for water emissions, and 13 of 20 points for solid waste disposal.

Time and Cost to Develop to Implementation Stage--

Combustion Engineering provided an estimate of 2 to 6 months for pilot plant testing at a cost of \$10,000 to \$200,000. Although the pilot plant does exist, this estimate appears to be optimistic, particularly in view of red water's high sodium content (see Appendix E). Ratings are 4 of 5 points for time and 3 of 5 points for cost.

Complexity of Process--

The process is fairly complex. Equipment includes an optional water evaporator, a high-temperature rotary kiln, a secondary incinerator, a scrubber, and a nitrogen oxide reduction system. The process will handle solids, gases, and liquids at high temperatures. The molten sodium salts will attack the rotary kiln refractory (see Appendix E). Process complexity, difficulty of operation, and flexibility of operating parameters are rated at 3 of 5 points. The evaluator's judgment is rated at 3 of 5 points because although the operating conditions are harsh and the estimated operation and maintenance costs will be high, the hardware and process have been proven at full scale and when the expected difficulties associated with red water have been overcome, a slag with reduced leaching characteristics will result.

3.2.9 Submerged Combustion

Theoretical Potential of the Process--

Submerged combustion is an established commercial technology. Although the indicated destruction efficiency of 99.99 percent may not destroy all of the color-forming nitroaromatics, it may be sufficient to qualify the effluent for delisting as a hazardous waste and treatment in a standard wastewater treatment facility. The rating is 9 of 10 points.

Current Application and Status of Technology--

Submerged combustion normally operates in a molten salt medium, and sodium attack on refractory may be a problem (see Appendix E). Although submerged combustion is an established full-scale technology for treatment of liquid organic wastes, it has not been used on red water or on a similar stream. The rating is 14 points of a possible 20.

Environmental Impact--

Environmental controls will be required for air, water, and possibly solid wastes. Air emissions will include sulfur dioxide, nitrogen oxides, and possibly particulate matter from rapidly decomposing organic nitro compounds. Wastewater from the caustic scrubber and the salt cake quench liquor may require treatment. The salt cake quench liquor may contain solids that require disposal as hazardous or toxic wastes. Submerged combustion operates at higher temperatures than conventional incinerators (at least 900°C, to keep sodium sulfate molten), and nitrogen oxide will be generated. The effectiveness of a caustic scrubber is limited in the control of nitrogen oxide emissions. The environmental emission problems can be resolved; however, resolution will require significant pilot-plant testing and engineering effort. Ratings are 6 of 10 points each for air and water emissions and 13 of 20 points for solid waste.

Time and Cost to Develop to Implementation Stage--

T-Thermal Inc., which has an existing 1×10^6 Btu/h pilot-plant quoted 3 months for pilot-plant testing and 12 additional months for a full scale design at a total cost of \$380,000. This quote appears to be optimistic when one considers that the pilot-plant unit will be operating with a feed that has not been run in the equipment before and that the feed differs a great deal from that for which the unit was designed (primarily covalent organic matter). The high sodium content may be a problem (see Appendix E). Sufficient operating experience will be needed to size and design a fairly elaborate emission control system and to define process operating parameters; therefore, ratings of 5 of 5 points are reduced to 4 of 5 points each for time and cost.

Complexity of Process--

Submerged combustion is a complex process. The process operates at a high temperature. Process streams include hot, corrosive gases, molten salts, potentially explosive organic nitro compounds, and possibly hot particulate matter. The quench and scrubber systems use significant quantities of water that will require treatment prior to discharge. A portion of this

water will be converted to steam. Emission controls for air and water will need to be designed, sized, and operated to fit the submerged combustion unit. The submerged combustion unit will have to operate under controlled conditions to minimize wear and damage to refractories and materials of construction. Ratings are 2 of 5 points for complexity of process and 3 of 5 points each for system operation, flexibility of operating parameters, and the evaluator's judgment.

3.2.10 Supercritical Water Oxidation

Theoretical Potential of the Process--

Supercritical water oxidation has proved to be effective in pilot-plant testing. A destruction efficiency of 99.10 percent is typical. This level of destruction may qualify the effluent for delisting and treatment in a conventional wastewater treatment system. Unfortunately, the SCWO process is not a highly conducive process with unstable waste streams. Significant safety concerns arise regarding the introduction of red water to temperatures in excess of 374°C and pressures above 212 atmospheres. Therefore, the rating is 6 of 10 points.

Current Application and Status of Technology--

Supercritical water oxidation has never been tested on red water or any similar stream. Successful tests of red water from Joliet Arsenal and the VAAP were run, however, with wet air oxidation, a technology that is similar except that wet air oxidation takes place at a lower temperature and pressure. Therefore, the rating is 10 of 20 points.

Environmental Impact--

Environmental impact awards are somewhat similar to those for wet air oxidation. Minimal air emissions should occur; therefore, the air emissions rating is 8 of 10 points. The wastewater may contain uncharacterized organic compounds as a result of partial combustion (although, theoretically, it should reflect a more complete destruction of organic compounds than that achieved by wet-air oxidation.) of red water organic compounds. The water emissions rating is 5 of 10 points. The wet air oxidation tests with red water indicate that no solids result from oxidation. Because this may not be the case for RAAP red water, the solid waste rating is 12 of 20 possible points.

Time and Cost to Develop to Implementation Stage--

Ratings are 3 of 5 points for time and 2 of 5 points for cost. Compared with wet air oxidation, the process reactions take place at higher temperatures and pressures; therefore, the developmental program should require more time and money. Both technologies have pilot-plant equipment available for testing.

Complexity of Process--

Compared with wet air oxidation, supercritical water oxidation operates at higher pressures and temperatures and is a less developed technology. Therefore, the ratings are 1 of 5 points for process complexity, 2 of 5 points for system operation difficulty, and 1 of 5 points for flexibility of operating parameters. The potential for more complete oxidation of organic compounds by SCWO over wet air oxidation would provide for an evaluator's judgment of 5 of 5 points; however, the safety factors alone require a reduction in the evaluator's assessment to 1 of 5 points.

3.2.11 Thermal Separation

Theoretical Potential of the Process--

Thermal separation is based on the concept that organic matter can be thermally decomposed in one stage and incinerated in a second stage. The sodium dinitrotoluene sulfonates are not particularly volatile; however, they may violently decompose in an unpredictable fashion. The theoretical potential rating is 3 of 10 points.

Current Application and Status of Technology--

Thermal separation has been demonstrated at full-scale on contaminated soils and organic solids; it has not been demonstrated on red water or liquids in general. The rating is 12 of a possible 20 points.

Environmental Impact--

Violent decomposition of red water nitro compounds could produce particulate and gaseous emissions. Solids from the first stage reactor will be water-leachable and may contain uncharacterized and toxic organic compounds. As described, the process collects nitrogen oxides in a scrubber and converts

them to nitric acid; nitrogen oxide (NO_x) conversion to nitric acid is about 95 percent in a commercial nitric acid plant. Recovery percentages would be much lower in a dilute stream with fluctuating NO_x compositions. Scrubbing is not a commercially accepted NO_x control method. The environmental impact ratings are 4 of 10 points for air emissions, 8 of 10 points for water emissions, and 10 of 20 points for solid waste. Major unresolved issues remain in the application of thermal separation for treatment of red water.

Time and Cost to Develop to Implementation Stage--

This technology has not been tested on any aqueous feed stream. Sodium attack on refractories may be a problem (see Appendix E). Also, a lengthy and expensive development program can be expected. Ratings are 1 of 5 points for time and cost.

Complexity of Process--

Two-stage thermal treatment with possible subsequent treatment of residual solids is a complex process. Operating parameters will have to be defined for both thermal treatment and the auxiliaries, and these operating parameters will probably be inflexible. Ratings are 2 of 5 points for process complexity and 1 of 5 each for difficulty of operation and flexibility of operating parameters. The evaluator's judgment rating is 0 of 5 points.

3.2.12 Circulating Bed Combustion

Theoretical Potential of the Process--

Circulating bed combustion has been demonstrated to be effective for the complete destruction of a variety of hazardous wastes. Establishing operating parameters and process controls for red water, which has a high sodium content, is possible but may require extensive development effort. The rating is 9 of 10 points.

Current Application and Status of Technology--

Full-size commercial units are in active service, and a pilot-plant-sized unit is available for research and development work. No work has been done on red water or any waste resembling red water. The rating is 13 of 20 possible points.

Environmental Impact--

The circulating-bed combustion technology could produce air emissions of sulfur oxides, nitrogen oxides, and particulate matter. Alkaline sodium salts (e.g., sodium oxide, sodium hydroxide, and sodium carbonate) produced by the thermal decomposition of sodium nitrate and sodium nitrite may adsorb most of the sulfur oxides, but they may also attack refractories (see Appendix E). Potential particulate matter emissions include sodium oxide, sodium hydroxide, sodium carbonate, sodium sulfite, and incompletely combusted organic matter. These particulates will vary in particle size and density and will be hot coming out of the combustor. A high-efficiency collector (e.g., fabric filter) will be mandatory. No water emissions should occur. Also, the ash should be readily disposable if it can be delisted as a hazardous waste or if at least 99.99 percent destruction is achieved. Ratings are 7 of 10 points for air emissions, 10 of 10 points for water emissions, and 12 of 20 points for solid waste.

Time and Cost to Develop to Implementation Stage--

A considerable (and costly) research and development effort will be required to adapt this technology to red water. This work may be performed offsite at Ogden Environmental Services' premises, or it may be preferable to build an onsite pilot plant at Radford. Combustion may produce large quantities of fines through decomposition of dinitrotoluene sulfonates; when water is evaporated, solid hydrated sodium sulfates may form, which explode like popcorn. Ratings are 3 of 5 points for time and 2 of 5 points for cost.

Complexity of Process--

Circulating bed combustion requires the combustion of solids and gases in a moving gas phase. Process and operation parameters will need to be defined before the amount of flexibility available can be ascertained. Tentative ratings are 3 of 5 points each for complexity of process, difficulty of operation, and flexibility of operating parameters. The process appears to be viable, and the evaluator's judgment is 4 of 5 points.

3.2.13 Sonoco Sellite Recovery Process

Theoretical Potential of the Process--

The Sonoco Sellite Recovery Process has been evaluated several times. The unanimous conclusion is that despite possible operating problems, the process is technically feasible. The rating is 9 of 10 possible points.

Current Application and Status of Technology--

A rating of 14 of 20 possible points has been applied based on the fact that significant portions of the process have been demonstrated in the laboratory and/or pilot plant on waste streams similar to RAAP red water.

Environmental Impact--

The air emission rating is 5 of 10 points. A proven commercial technology is available to control all process emissions; however, additional process development work is required to size and design the emission controls properly.

The wastewater discharge rating is 5 of 10 points. The process requires the recycling of the water effluent. The points are reduced because the impact of recycling this stream has not been addressed. Impurities buildup may require additional treatment before the aqueous effluent can be recycled or discharged.

The solid waste rating is 15 of 20 points. The red water ash, petroleum coke ash, and eroded furnace refractory are sources of solid wastes that require disposal and possible treatment.

The Sonoco Sellite Recovery Process recycles the effluent and has been given a recyclability rating of 8 of 10 points. The reduction in points is because the consequences of continuous recycling have not been addressed.

Time and Cost to Develop to Implementation Stage--

As several evaluators have pointed out, significant additional R&D is needed for the proper design of a commercial facility. The rating is 2 of 5 points for time. A capital cost estimate for the facility (dated May 1984) indicated \$28 million. For the scope of this project, an R&D budget of at least \$1 million seems reasonable. The cost rating is 1 of 5 points.

Complexity of Process--

Process complexity is rated at 1 of 5 possible points. The furnace operates at 1750°F, and the operating scheme is such that separate zones are used to produce both reduced and oxidized output. Both liquid and gas process streams contain suspensions of abrasive solids that also require very clean separations. The material is recycled, and a buildup of impurities is possible. Many of the process complexities are still unresolved. Difficulty of operations is rated at 1 of 5 points. Points are deducted for the simultaneous operation of a single furnace in an oxidizing and reducing mode, high-temperature processing of organic nitro compounds that may be explosive, and the numerous operations that require phase separations.

Flexibility of operating parameters is rated at 1 of 5 points. The point deduction is due to process complexity and many undefined operating parameters. The evaluator's judgment rating is 1 of 5 points. This red water incineration process has been made much more complex and costly to achieve sodium sulfite (sellite) recyclability.

3.2.14 Argonne National Laboratory Process

The Argonne National Laboratory (ANL) process is the least developed of the technologies evaluated in this section. Single-stage test-tube-scale experiments have demonstrated that red water organics are preferentially extracted into polyethylene glycol (PEG) solution. The ANL has tested fungi that can survive in red water. In their experiments, best results were obtained when glucose was added as a supplemental nutrient. They have not yet demonstrated that any of the fungi or enzymes derived from the fungi-digested red water instead of the glucose.

This work is a shift in direction from the process receiving preliminary evaluation (presented in Appendix C). Appendix F presents the findings revealed in a meeting with ANL staff, during which the present status and projected future developments of the technology as presented by ANL were reviewed.

Theoretical Potential of the Process--

The ANL process is rated as 5 of 10 points for theoretical potential. The deduction in points is due to the preliminary status of the technology

and major unresolved issues that must be addressed (e.g., the efficient recovery and recycling of the polyethylene glycol and the development of a biological medium that quantifiably destroys red water organics).

Current Application and Status of Technology--

Single-stage test-tube-scale experiments have demonstrated that red water organic compounds are preferentially extracted into PEG solution. Also, fungi that survive in red water have been found, but supplemental nutrients (glucose) are necessary. This is far short of satisfying the criteria, which states "...small portion of the process has been demonstrated in the laboratory or pilot plant" (10 points). The rating is 6 of 20 points.

Environmental Impact--

The ANL process is not well enough defined to predict either the potential emissions or what measures would be required to control these emissions. The fundamental, but yet-to-be-demonstrated, approach of the ANL process is to separate red water into organic and inorganic fractions and to treat each fraction separately. Assuming that this can be accomplished, red water processing will produce no solid wastes. Air emissions should be limited to NO_x emissions from the acidification of sodium nitrite (these emissions would be much less than those produced by any red water incineration process) and possibly VOCs formed by the biological decomposition of red water organics. The air emissions rating is 9 of 10 points. Wastewater from the treatment of the organic and inorganic constituents of red water would be the principal process effluent. Because of the lack of definition of required measures, the rating is 3 of 10 possible points. The solid waste rating is 14 of 20 points.

Time and Cost to Develop to Implementation Stage--

The current status of the technology represents 6 months work costing \$200,000. Projected progress is largely guesswork, but a rating of 2 of 5 points for time (ANL's initial development schedule was four years) and a rating of 1 of 5 points for cost have been applied.

Complexity of Process--

The ANL process is quite complex. First, the red water has to be separated into organic and inorganic fractions, which are then treated

separately. All of this technology has yet to be developed. Also, even if solvent extraction is successful for separating red water into organic and inorganic fractions, the PEG extractant must be recovered and recycled while PEG losses are held to economically acceptable levels. The ANL has suggested ultrafiltration as a means of separating PEG from the aqueous salt solution, but this has yet to be demonstrated. Furthermore, the ultrafiltration technology did not survive the preliminary evaluation for red water treatment. Ratings of 1 of 5 points each have been applied for process complexity, difficulty of operation, and flexibility of operating parameters. The evaluator's judgment rating is 0 of 5 points because of the multitude of technical questions that must be resolved.

3.3 PRESENTATION OF RESULTS

Table 3-3 presents comparative evaluations of the evaluated red water treatment technologies in the order in which they were presented. Table 3-4 lists the technologies in descending order of their quantitative rating based on the five evaluation criteria and 110-point scale. The four highest rated technologies and their ratings are as follows:

°	Wet air oxidation	73
°	Circulating-bed combustion	69
°	Slagging rotary kiln	68
°	Submerged combustion	66

The four highest rated technologies all received 9 out of 10 possible points for theoretical potential (the SSRP was the only other technology to receive 9 points for theoretical potential) and at least 13 of 20 points for current application of technology. These ratings indicate that these technologies are expected to be applicable to red water treatment and have already been used effectively as a complete system on waste streams somewhat similar to red water.

Of primary importance is the ability of the treatment technologies to produce environmentally acceptable waste streams. Of the top four rated technologies, wet air oxidation received 9 of 10 possible points for air emissions, whereas the three thermal treatment processes were slightly lower air emissions ratings (6 and 7). Wet air oxidation laboratory studies with red water in 1956 did not indicate the occurrence of air emissions. The

TABLE 3-3. COMPARATIVE EVALUATIONS OF RED WATER TREATMENT TECHNOLOGIES^a

Technology	Theoretical potential of the process (10)	Current application of technology (20)	Environmental impact, air (10), wastewater (10), solid waste (20), recyclability (10), total (50)				Time and cost to develop to implementation stage (5 each, 10 total)		Complexity of process, difficulty of operation, process flexibility, evaluator's judgement (5 each, 20 total)					Total (110)
			Air	Waste-water	Solid waste	Recyclability	Time	Cost	CP	DO	PF	EJ		
White rot fungus on packed bed reactor	8	7	10	3	4	0	3	3	3	4	3	3	51	
Catalyzed wet oxidation	4	7	4	2	17	2	3	3	2	1	2	1	46	
Liquid phase oxidation	6	7	7	3	17	0	2	2	2	3	3	1	53	
Solids precipitation with surfactants	7	7	6	0	0	0	2	2	1	1	1	0	27	
Wet air oxidation	9	14	9	5	16	0	4	3	2	3	3	5	73	
Hybrid thermal treatment system	8	16	5	5	7	0	4	4	2	2	2	2	57	
Plasma arc	5	11	9	9	17	0	3	2	3	2	2	1	64	
Slugging rotary kiln	9	14	6	6	13	0	4	4	3	3	3	3	68	
Submerged combustion	9	14	6	6	13	0	4	4	2	3	2	3	66	
Supercritical water oxidation	6	10	8	5	12	0	3	2	1	2	1	1	51	
Thermal separation	3	12	4	8	10	0	1	1	2	1	1	0	43	
Circulating bed combustion	9	13	7	10	12	0	3	2	3	3	3	4	62	
Sonoco Sellite Recovery	9	14	5	5	15	8	2	1	1	1	1	1	63	
Argonne National Laboratory process	5	6	9	3	14	0	2	1	1	1	1	0	43	

^a Maximum point awards are shown in parentheses.

thermal processes are known to generate air emissions; however, with the proper controls, they can be readily managed (thus, the slight reduction in assigned points for air emissions). Of the thermal technologies, circulating-bed combustion received a higher air emissions ranking because less air is used in the process, which reduces the size of air emissions controls needed.

TABLE 3-4. RANKING OF EVALUATED TECHNOLOGIES IN DESCENDING ORDER OF QUALITATIVE EVALUATION

Ranking	Technology	Quantitative point assessment (110 points available)
1	Wet air oxidation	73
2	Circulating-bed combustion	69
3	Slagging rotary kiln	68
4	Submerged combustion	66
5	Plasma arc	64
6	Sonoco sellite recovery	63
7	Hybrid thermal treatment system	57
8	Liquid-phase oxidation	53
9	White rot fungus on a packed bed reactor	51
10	Catalyzed wet oxidation	48
11	Thermal separation	43
12	Argonne National Laboratory process	43
13	Solids precipitation with surfactants	27

The higher ratings for wastewater emissions were assigned to the thermal technologies because the generated wastewaters would result primarily from scrubbers and spraying. The circulating-bed combustion process received 10 of 10 wastewater emission points because no wastewaters should be generated during operation. Wet air oxidation received the lowest wastewater rating (5 of 10 points) of the top four technologies because the effluent from this process will require further treatment for solids removal and the wastewater will have to be delisted or classified as no longer reactive before its discharge.

Solid wastes generated by previous laboratory-scale wet air oxidation tests on red water generated ferric oxide. Because the constituents of the red water used in the wet air oxidation laboratory studies in 1956 differed significantly with the current understanding of red water constituents, what solids may be generated is unknown.

As would be expected, the ash resulting from the thermal processes reduced their solid waste point assignment to a rating below that for wet air oxidation. Because the slagging rotary kiln and submerged combustion process (13 of 20 points each) operate at higher temperatures than conventional incineration processes, a slag is generated upon solidification of the molten salts, which encapsulates the constituents and reduces the leachability of the overall solid residual. The circulating-bed combustion process does not operate at the higher temperatures; therefore, an ash rather than slag is formed. The ash is more susceptible to leaching than is the slag; thus, the circulating-bed combustion process received 12 instead of 13 points for solid waste.

The time and cost for developing each of the top four rated technologies depended more on the immediate availability of bench- or pilot-scale facilities where treatability tests with actual red water could be performed. Small-scale test facilities are available for all four of the top-rated technologies. The circulating-bed combustion process received a slightly lower time and cost ratings (3 of 5 vs. 4 of 5 and 2 of 5 vs. 3 or 4 of 5, respectively) because of the lower number of actual operating facilities from which operation and performance information could be obtained.

All of the true thermal (incineration) treatment technologies scored consistently in a range of 57 to 69 points; average point assignment was 64.5 and the standard deviation was 4.3. The overall range of the 14 technologies evaluated was 27 to 73 points, with an average of 55.4 and a standard deviation of 12.75. Thus, all of the true thermal treatment technologies were rated as above the average of all the evaluated technologies. This confirms the consistency of the subjective point assignment inasmuch as the thermal technologies all have the same types of primary problems, which are as follows:

- ° Slagging and damage to refractory walls because of high salt content.
- ° Production of NO_x and SO_x .
- ° Generation of a residual ash that is highly leachable.

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

The four technologies with the highest point ratings appear technically feasible to meet the environmental regulations for the treatment of red water and are recommended for further evaluation. This section summarizes the strengths and limitations of each of the four technologies, suggests an approach for performing actual treatability tests, and discusses a potential short-term RAAP red water disposal method for consideration when final technology evaluations are performed with actual RAAP red water.

4.1 WET AIR OXIDATION

4.1.1 Strengths

The strengths of wet air oxidation as a treatment process for red water include the following:

- ° In previous laboratory studies (1956) using red water, COD was reduced by 97.1 percent.
- ° Improvements to the technology and equipment have been made since the study in 1956.
- ° Wet air oxidation of toxic wastes has produced effluent streams with better than 95 percent oxidation of organic matter and a waste stream that can be handled by a conventional wastewater treatment plant.
- ° In numerous instances, this technology has been used successfully to treat other toxic wastes.
- ° Sulfites are oxidized to sulfates and nitrites are oxidized to nitrates, which reduces the potential for sulfur dioxide and nitrogen oxide emissions.
- ° Capital and O&M costs are low compared with the other technologies.
- ° Laboratory facilities are readily available to perform treatability studies.

4.1.2 Limitations

The limitations for wet air oxidation as a treatment process for red water are as follows:

- ° Effluent from the wet air oxidation process will require further treatment prior to its discharge.
- ° Treated red water will require delisting.
- ° Previous studies with red water did not identify residual COD.
- ° Numerous unknown operating parameters for red water treatment will require investigation.

4.2 CIRCULATING BED COMBUSTION

4.2.1 Strengths

The strengths of circulating-bed combustion as a treatment process for red water include the following:

- ° Highly efficient combustion of organics eliminates the need for a downstream afterburner.
- ° The system performs dry scrubbing in combustor, which eliminates the need for a wet scrubber, which would generate dilute acids.
- ° The system operates at subatmospheric pressure, which prevents leakage or escape of hazardous materials.
- ° High destruction efficiencies in the combustor reduce excess air requirements to 30 to 40 percent, which reduces the quantity of the only generated air pollutant, NO_x .
- ° Two full-scale transportable units are currently in operation, and two more are nearing completion of construction.
- ° A pilot-scale system is readily available in San Diego, California. The pilot system operates at 600 lb liquid per hour (approximately 1.2 gpm).

4.2.2 Limitations

The limitations for circulating-bed combustion as a treatment process for red water are as follows:

- ° It is a proprietary technology.

- Combustion of red water requires auxiliary fuel.
- The process generates an ash that is potentially susceptible to leaching and will require ultimate disposal.
- Process byproducts would require delisting.
- Only a limited number of units are currently in operation.
- Existing full-scale units neither have nor are now treating waste-waters similar to red water.
- Scaleup/down factors are unknown.
- Pilot-scale demonstrations are estimated to cost between \$60,000 and \$250,000, depending on the exact nature of testing and analytical requirements.

4.3 SLAGGING ROTARY KILN

4.3.1 Strengths

The strengths of the slagging rotary kiln as a treatment process for red water include the following:

- Higher operating temperatures enable more complete combustion of wastes and provide encapsulation of constituents in the slag.
- The generated slag is less susceptible to leaching than is the ash from conventional incineration.
- The technology has been used effectively throughout the United States and Europe on more than 10,000 wastes and has generally achieved greater than 99.99 percent removal efficiency.
- The potential exists for finding an operating unit where treatability tests on red water could be performed.

4.3.2 Limitations

The limitations of the slagging rotary kiln as a treatment process for red water are as follows:

- Operating temperatures are greater than those for conventional incinerators; thus, fuel consumption is higher and wear on the refractory is greater.
- Extensive pretreatment is required to concentrate solids prior to their introduction to the incinerator.

- ° A secondary combustion chamber is required.
- ° Effluent wastewaters from the scrubber and quench tank require characterization and treatment.
- ° The process has not been tested with red water.
- ° Process byproducts will require delisting.
- ° The process entails higher capital costs, greater energy and fuel consumption, and greater O&M costs.
- ° No known pilot-scale SRK system is available for treatability studies.

4.4 SUBMERGED COMBUSTION

4.4.1 Strengths

Submerged combustion is similar to the slagging rotary kiln in that it operates at temperatures higher than those in a conventional incinerator. The operating temperature is high enough to melt the salts that are formed in the process. The strengths of submerged combustion as a treatment process for red water include the following:

- ° High operating temperatures melt salts formed in the process.
- ° Molten salts are easily removed from furnace.
- ° High saline solution from the molten salt quench bath can be discharged to a conventional wastewater treatment plant.
- ° The process is well suited for liquid wastes and has already achieved 99.99 percent reduction of numerous organic compounds.
- ° A pilot-scale facility is readily available for its evaluation as a red water treatment.
- ° Process is in use at various scales in approximately 116 locations throughout the world, which provides an extensive baseline of previous experience from which to draw.

4.4.2 Limitations

The limitations of submerged combustion as a treatment process for red water are as follows:

- ° Operating temperatures are greater than those for conventional incinerators; this results in higher capital costs, greater energy and fuel consumption, increased wear on refractory, and higher O&M costs.
- ° Pretreatment is required to concentrate solids prior to their introduction to the combustor.
- ° A secondary combustion chamber is required.
- ° Effluent gas will require particulate removal, gas neutralization, and NO_x and SO_x reduction.
- ° Quench bath of molten salts yields a highly saline solution that will require additional treatment.
- ° Byproducts of process will require delisting.
- ° The process has not been tested with red water.
- ° Pilot-scale demonstrations are estimated to cost between \$20,000 and \$80,000, depending on the tests performed and analytical requirements.

4.5 PROPOSAL FOR TREATABILITY STUDIES

The United States does not currently produce domestic TNT; therefore, no red water is generated from which samples can be collected for treatment evaluation. Also, no red water exists in storage from any previous domestic TNT production activities. As a result, a suitable surrogate wastewater stream must be selected. Within the United States, obtaining black liquor from the pulp and paper industry is one possibility. Previous studies on black liquor and red water have led to the conclusion that the two waste streams contain similar constituents. The major difference is that black liquor has a much higher Btu rating than does red water. Thus, although byproduct and wastestream characteristics and the posttreatment requirements could be readily identified and subsequently determined for red water, actual operating parameters of the system when used for the treatment of black liquor would not be comparable to those required for the treatment of red water.

As an alternative, sufficient red water could be obtained for treatment evaluations from the currently operating Canadian Industrial Limited (CIL)

TNT production facility. The United States uses TNT produced by the CIL process, and it has been determined that although the red waters generated from the various U.S. facilities and CIL are not exact, they are quite similar. Thus, until one of the domestic U.S. TNT production facilities is taken out of mothballs and started up again, CIL red water represents the most similar and suitable waste stream for technology treatability evaluations. Use of CIL-generated red water would allow for red water treatment evaluation. Preliminary screening of the effectiveness of the technology for domestic treatability evaluations could be performed at the pilot-scale facilities of the respective technology vendors. From these preliminary treatability screenings, the most feasible of the technologies could be evaluated and costed out further. Prior to the design and installation of a red water treatment system, additional pilot-scale treatment studies should be performed with red water from the TNT plant for which the treatment technology is being proposed.

4.6 TECHNOLOGY TREATABILITY EVALUATIONS WITH DOMESTIC TNT RED WATER AND POTENTIAL SHORT-TERM TREATMENT/DISPOSAL OPTION FOR RAAP-GENERATED RED WATER

As stated previously, domestic U.S. TNT production facilities will not be started back up to meet peace-time TNT demands until a suitable red water treatment technology has been identified and is in place to treat generated red water. Also, it has been recommended that a red water treatment facility not be installed until it has been tested with red water from the actual TNT production facility for which it is intended. These two constraints generate a "catch 22" dilemma. The preceding subsection discussed the potential for preliminary technology treatability screenings with CIL red water to determine the feasibility of the technology for red water treatment. This subsection describes how the surviving (top rated) technology(s) from the preliminary treatability screenings might be evaluated with red water from the actual TNT production facility for which it is intended, prior to implementation at that facility, without discharging unacceptably treated red water.

The RAAP TNT production lines have been considered the most likely candidates for startup if and when domestic TNT production is resumed to meet peace-time TNT demands. Thus, it would appear that the first red water treatment systems is intended for the RAAP facility. Should RAAP TNT

production lines be started up to generate red water for final pilot-scale technology evaluations, it is assumed that they will continue to run, at least for a short while, to restock depleted TNT supplies inasmuch as the cost of startup is expected to be high. The pilot-scale treatment facilities will not be capable of treating all of the generated red water; therefore, a short-term treatment/disposal alternative for RAAP red water needs to be identified for the excess red water that will be generated during treatment evaluations, system design, and construction. Identifying a short-term treatment/disposal option would also allow for production of domestic TNT to begin immediately.

The short-term red water treatment/disposal alternative may be to ship the RAAP red water to du Pont's Deepwater, New Jersey wastewater treatment facility. On March 14, 1990, PBMA had CIL red water samples sent to du Pont for an evaluation of treatment through the Deepwater wastewater treatment facility. At the time this report was finalized, results of these evaluations were not available. Should the evaluations prove that the du Pont Deepwater facility can satisfactorily treat red water, the U.S. Army could enter into a short-term agreement with du Pont for RAAP red water treatment. Investigations into the potential licensing of the technology for possible implementation at RAAP could also be considered.

REFERENCES

- Brown, M. A. 1987. The Clean Water Act as Amended by the Water Quality Act of 1987. Practicing Law Institute.
- Eckenrode, J., G. Denzler, and J. Klein. 1980. Evaluation of TNT Red Water Pollution Abatement Technologies. Final Report. U.S. Army Armament Research and Development Command, Chemical Systems Laboratory, Environmental Technology Division. Technical Report ARCSL-TR-90023.
- Gilbert, E. E., et al. 1982. New Procedures for Purifying TNT. Propellants, Explosives, Pyrotechnics, 7:160-164.
- Goldberg, R. E. 1988. Long-Term Study Plan for Red Water Treatment. U.S. Army Production Base Modernization Activity, Picatinny Arsenal. AMSMC-PBE-C, AV 800-4076.
- Helbert, W. B., Jr., E. Pregun, and J. A. Carrazza. 1983. Recovery of Sellite from TNT Red Water. U.S. Army Armament Research and Development Contractor Report ARLCD-CR-82010. Command, Large Caliber Weapon Systems Laboratory, Dover, New Jersey.
- Peters, M. S., and K. D. Timmerhaus. 1980. Plant Design and Economics for Chemical Engineers. 3rd ed. McGraw-Hill Book Company, New York.

APPENDIX A

TNT PRODUCTION CAPACITIES, RAAP RED WATER ANALYSIS, AND POLLUTION CONTROL REQUIREMENTS

Table A-1 presents nominal TNT production capacities at the five North American TNT plants. Of these plants, only the Canadian Industries Limited (CIL) plant is now in production. Of the four currently idle plants, the Radford, Virginia, plant is the best candidate for reactivation. Table A-1 also presents potential red water volumes generated at each plant.

Table A-2 presents representative analyses of Radford Army Ammunition Plant (RAAP) red water. These analyses include identification of the inorganic and organic solids dissolved in red water. The Alpha-TNT sellite complex and the TNT sodium sulfonates are all sodium dinitrotoluene sulfonates; none of these molecules have three nitro groups on the benzene ring.

Table A-3 presents the air, water, and solid waste discharge standards applicable to RAAP. These standards could have an impact on the choice of a red water treatment technology.

TABLE A-1. PRODUCTION CAPACITIES AND POTENTIAL RED WATER GENERATION BY
NORTH AMERICAN TNT PLANTS^a

Producer	TNT capacity, tons/day (nominal)	Red water generated, gallons/day (15% solids)
Radford AAP	100 continuous	16,250
Joliet AAP	300 continuous 500 batch (either/or both)	48,750 81,250
Volunteer AAP	300 continuous 250 batch	48,750 40,625
Newport AAP	250 continuous	40,625
Canadian Industries Limited	35 continuous	5,687

^a The Canadian Industries Limited facility is the only plant currently in production.

Source: Review of Canadian Industries Limited's Boloeil Facility as a Candidate Site for a SRP Pilot Test. Radford Army Ammunition Plant, October 26, 1988.

**TABLE A-2. REPRESENTATIVE ANALYSES OF
RADFORD ARMY AMMUNITION PLANT (RAAP) RED WATER**

Percent solids	15% nominal
Water content	85% nominal
pH	7.0 - 9.7
Color	Dark red
Sp.G.	1.1 nominal
Dry solids	Will burn
Solids heat value	Variable (3200 Btu/lb nominal)
 Metal content, mg/L	
Calcium	346
Iron	307
Magnesium	90
Potassium	42
Aluminum	10
Chromium	4.94
Barium	3.0
Copper	2.30
Cadmium	0.66
Silver	0.40
 Inorganic salts, wt. percent	
Na_2SO_3 - Na_2SO_4	32.3
NaNO_2 (sodium nitrite)	11.2
NaNO_3 (sodium nitrate)	1.5
Sodium sulfide (NaHS - Na_2S)	May be present
Sodium carbonate/bicarbonate	May be present
Subtotal inorganic salts	45.0
 Nitrobodyes, wt. percent	
Sodium sulfonate of 2,4,5-TNT	22.7
Alpha-TNT-Sellite complex	16.2
Sodium sulfonate of 2,3,4-TNT	9.6
Sodium sulfonate of 2,3,6-TNT	2.0
Sodium sulfonate of 2,3,5-TNT	Trace
2,4,6-TNBA (trinitrobenzoic acid) sodium salt	1.0
White compound sodium salt	1.0
TNBAL-bisulfite addition compound (trinitrobenzaldehyde)	1.0
TNBOH (trinitrobenzyl alcohol)	1.0
Sodium nitroformate	0.5
3,4-DNBA (dinitrobenzoic acid) sodium salt	Trace
2,3-DNBA (dinitrobenzoic acid) sodium salt	Trace
TNB (trinitrobenzene)-Sellite complex	Trace
Dissolved 2,4-DNT (dinitrotoluene)	Trace
Dissolved a-TNT (trinitrotoluene)	Trace
Subtotal nitrobodyes	55.0
Total wt. percent	100.0

Source: Review of Canadian Industries Limited's Bolsoell Facility
as a Candidate Site for a SRP Pilot Test. Radford Army
Ammunition Plant, October 26, 1988.

TABLE A-3. RAAP POLLUTION CONTROL REQUIREMENTS

	<u>Deminimus level, tons/yr</u>
<u>AIR</u> (SRP or other new red water abatement facility):	
Carbon monoxide	100
Oxides of nitrogen	40
Sulfur dioxide	40
Particulates	25
Ozone	40
Acid mist	7
Total reduced sulfur compounds (as H ₂ S)	10

LIQUID (to New River):

pH = 6-9 (each outfall)
 Temperature = 32°C max. in summer (each outfall)
 25°C max. in winter (each outfall)
 N (from all compounds) ≤ 6600 kg/day average for total plant
 (500 kg/day max. allocated for SRP)
 SO₄ ≤ 50,000 kg/day average for total plant
 (5000 kg/day maximum allocated for SRP)

SOLIDS (e.g., ash to landfill):

No hazardous wastes may be landfilled.

Any solids landfilled must contain no nitrobody, must pass test for reactivity, and must pass EP toxicity test SW-846 for metals.

Ba ≤ 100 mg/L	Pb ≤ 5 mg/L
Ag ≤ 5 mg/L	Cd ≤ 1 mg/L
As ≤ 5 mg/L	Se ≤ 1 mg/L
Cr ≤ 5 mg/L	Hg ≤ 0.2 mg/L

Source: Review of Canadian Industries Limited's Boloeil Facility as a Candidate Site for a SRP Pilot Test. Radford Army Ammunition Plant, October 26, 1988.

APPENDIX B
- NOT USED -

APPENDIX C

PRELIMINARY EVALUATIONS OF WASTEWATER DISPOSAL PROCESSES; TECHNICAL DISCUSSIONS AND DECISION TREES

CONTENTS

<u>Technology</u>	<u>Page</u>
Biodegradation by British Royal Ordnance	C-2
Biodegradation by White Rot Fungus on a Packed Bed Reactor	C-4
Biodegradation by White Rot Fungus on a Rotating Biological Contactor (RBC)	C-7
Composting	C-10
Land Treatment	C-13
Acidification	C-15
Carbon Adsorption	C-18
Catalyzed Wet Oxidation	C-22
Freeze Technology	C-25
Ion Exchange	C-28
Liquid Phase Oxidation	C-33
Reverse Osmosis	C-37
Stabilization/Solidification	C-43
Surfactant Technology	C-47
Wet Air Oxidation	C-51
Fluidized Bed Reduction of Incineration Ash	C-54
Hybrid Thermal Treatment System (HTTS)	C-58
Incineration by Canadian Industries Limited at Beloeil Works	C-62
Plasma Arc	C-67
SCA Billerud Recovery	C-70
Slagging Rotary Kiln	C-73
Submerged Combustion Process	C-76
Supercritical Water Oxidation	C-79
Tampella Recovery Process	C-83
Thermal Separation	C-87
Ammonium Sulfite Purification	C-91
Magnesium Sulfite Purification	C-94
Nitric Acid Purification	C-97
Argonne National Laboratory Process	C-100
Licensing Existing Industrial Technology	C-107
Sonoco Sulfite Recovery Process	C-111
References for Appendix C	C-115

BIODEGRADATION BY BRITISH ROYAL ORDNANCE

British Royal Ordnance (BRO) stated in early 1988 that the results of research on the use of bacteria to degrade red water, conducted in association with a local university, appeared promising, according to a draft report by Foster Wheeler on disposal alternatives for red water. At that time, the project was in an early stage of development.

We were unable to contact British Royal Ordnance for the preliminary evaluations. Further attempts to contact them will be made during the secondary-level evaluations.

The prescreening decision tree for biodegradation by British Royal Ordnance is shown in Figure A-1, and the decision tree analysis is provided below.

- ° Is the technology compatible with red water? Unknown. Contact has not yet been made with the researchers.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The process would be conducted on red water, which is an effluent from the TNT purification process.
- ° Is the process a concentrative rather than a treatment effort? No. The biological process would presumably degrade the organic constituents of red water.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to post-treatment for same? Unknown. However, if the process were successful, the effluent would be suitable for discharge.

Due primarily to the lack of information currently available, biodegradation by BRO has survived the Go/No-Go evaluation so that attempts to contact BRO can be extended.

BIODEGRADATION BY BRITISH ROYAL ORDNANCE

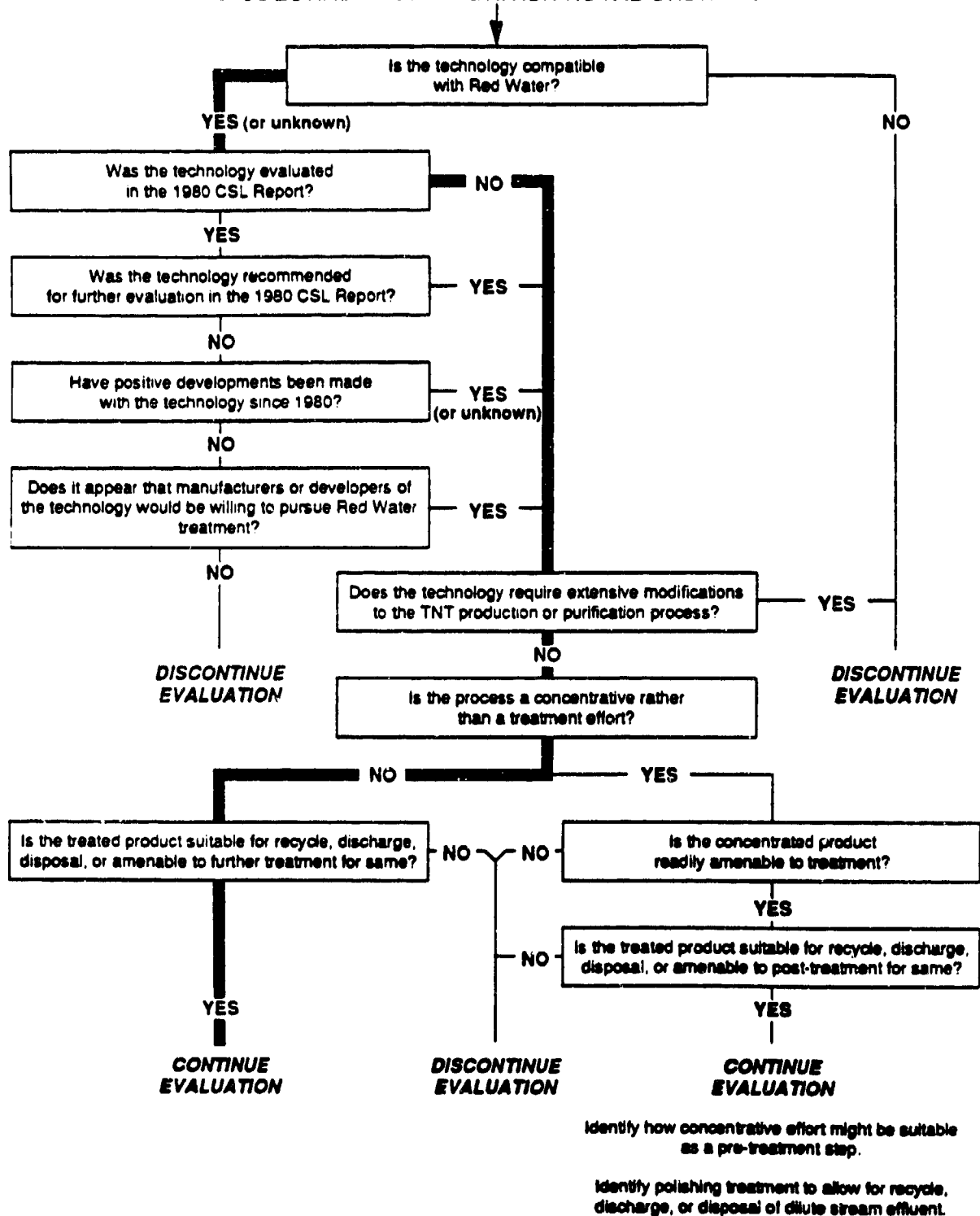


Figure A-1. Prescreening decision tree for biodegradation by British Royal Ordnance.

BIODEGRADATION BY WHITE ROT FUNGUS ON A PACKED BED REACTOR

At the New Jersey Institute of Technology (NJIT), Gordon Lewandowski is evaluating a packed bed reactor configuration for degradation of chlorinated phenols, primarily 2-chlorophenol, by white rot fungus (Evans, 1989). The packed bed consists of a porous, silica-based diatomaceous earth (produced by Manville Remedial, Colorado). Fungi migrate into the 20 micron interior of the diatomaceous earth. The columns are 3 feet high and 4 inches wide, and operate in an upflow mode with an oxygen sparger at the bottom. The surface area/volume ratio afforded by this setup is up to 1000 times higher than that of the rotating biological contactor (RBC). Researchers at NJIT are currently working on optimization of oxygen distribution and measurement of enzyme production. The packed bed reactor has no moving parts.

Dr. Daniel Siciu of CE Environmental, Inc., also believes that packed beds have a much higher efficiency than RBCs, and says CE Environmental switched their research focus to a packed bed process similar to that of NJIT as of fall 1989 (Siciu, 1989). Using synthetic pink water (by dissolving TNT in tap water) in a column with a holdup of 170 ml, results so far have indicated a potential TNT reduction of 97.8 percent.

The prescreening decision tree is shown in Figure A-2 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. The tests described above were conducted on dissolved TNT in tap water. Red water, however, consists primarily of impurities such as dinitrotoluene sulfonate salts, and has only trace amounts of dissolved TNT.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No.
- ° Is the process a concentrative rather than a treatment effort? No.

BIODEGRADATION BY WHITE ROT FUNGUS IN A PACKED BED REACTOR

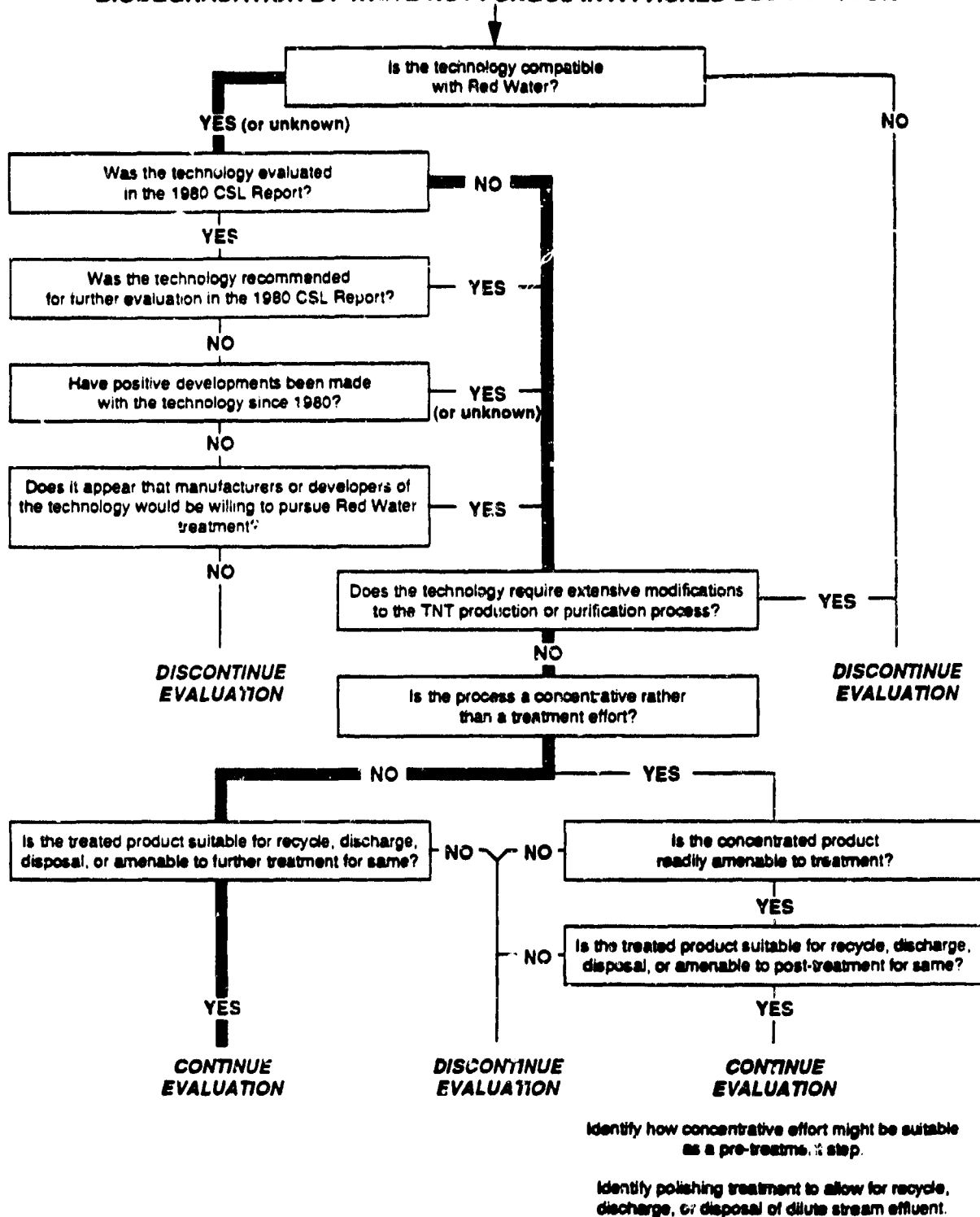


Figure A-2. Prescreening decision tree for biodegradation by white rot fungus in a packed bed reactor.

- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. If successful, the effluent would be suitable for discharge.

In view of the above information, white rot fungus on a packed bed reactor may be compatible with treatment of red water and is recommended for further evaluation.

BIODEGRADATION BY WHITE ROT FUNGUS ON A ROTATING BIOLOGICAL CONTACTOR (RBC)

White rot fungus is a ubiquitous organism in nature that degrades wood lignin. Lignin has a high molecular weight and contains significant numbers of aromatic nuclei. The white rot fungus has been shown to degrade a variety of nitro and chlorinated organic compounds, including PCP, TCP, TNT, RDX (cyclotrimethylenetrinitramine), dioxins, lindane, and DDT. After initial culture of the fungus in a well defined, enriched nutrient medium, the fungus is induced to degrade recalcitrant compounds by modifying nutrient conditions so that it enters a "secondary metabolic" phase. In the secondary or lignolytic phase the fungus synthesizes and excretes a family of nonspecific enzymes that is capable of oxidative cleavage of C-C bonds in sidechains, and oxidative cleavage of aromatics.

A rotating biological contactor (RBC) inoculated with white rot fungus has been used successfully to treat pink water containing 150 mg/l TNT and 70 mg/l RDX (Joyce, 1987). An RBC was chosen for evaluation of the white rot fungus because the fungus seems to function better in attached growth (fixed film) reactors than in the suspended growth mode. In batch and continuous flow tests, the fungus decomposed TNT essentially completely and degraded RDX by 90%. No significant sludge problem exists because the fungus does not grow significantly while in secondary metabolism. The entire process overview is as follows:

1. Equalizer/Settler
2. Biotreatment by RBC
3. Clarifier
4. Sludge dewatering
5. Dual media filter
6. Carbon filter

All the RBC evaluations were conducted using natural pink water. The RBC had a holdup of 2000 ml. At a flow rate of 1.6 ml/min, TNT concentrations

were reduced from 91 to 20 ppm. The limit of solubility for TNT in water is approximately 250 mg/l, and the total concentration of nitroderivatives in pink water is approximately 200 mg/l. The concentration of TNT plus related impurities in red water is much higher, in the range of 10 to 20 percent.

Biological degradation of particulate TNT is probably not reasonable. However, for wastewater containing high concentrations of TNT and related impurities, placement of a biological treatment step in a process train following clarification of a high-suspended-solids waste may be a relatively cost effective and permanent solution to disposal of the clarified effluent.

Plans are now underway by EPA to conduct pilot-scale demonstrations of this technology (Glaser, 1989). Dr. Thomas Joyce of North Carolina State University, which holds the patent for this process, suggests that evaluation of activated carbon as a fixed film substrate for growth of the white rot fungus would be worthwhile (Joyce, 1989). In such a case, the activated carbon would immediately adsorb contaminants from wastewater and hold them while the fungus degraded the contaminants and, in effect, acted as an on-going regeneration mechanism for the carbon.

The prescreening decision tree is shown in Figure A-3 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. The tests described above were conducted on pink water, which consists chiefly of alpha TNT dissolved in water. Red water, however, consists primarily of impurities such as dinitrotoluene sulfonate salts, and has only trace amounts of dissolved TNT and DNT.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No.
- ° Is the process a concentrative rather than a treatment effort? No.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. If successful, the effluent would be suitable for discharge. The sludge problem would be minimal since the fungus does not grow significantly during secondary metabolism.

In view of the above information, white rot fungus on an RBC may be compatible with treatment of red water and is recommended for further evaluation.

BIODEGRADATION BY WHITE ROT FUNGUS ON A ROTATING BIOLOGICAL CONTACTOR

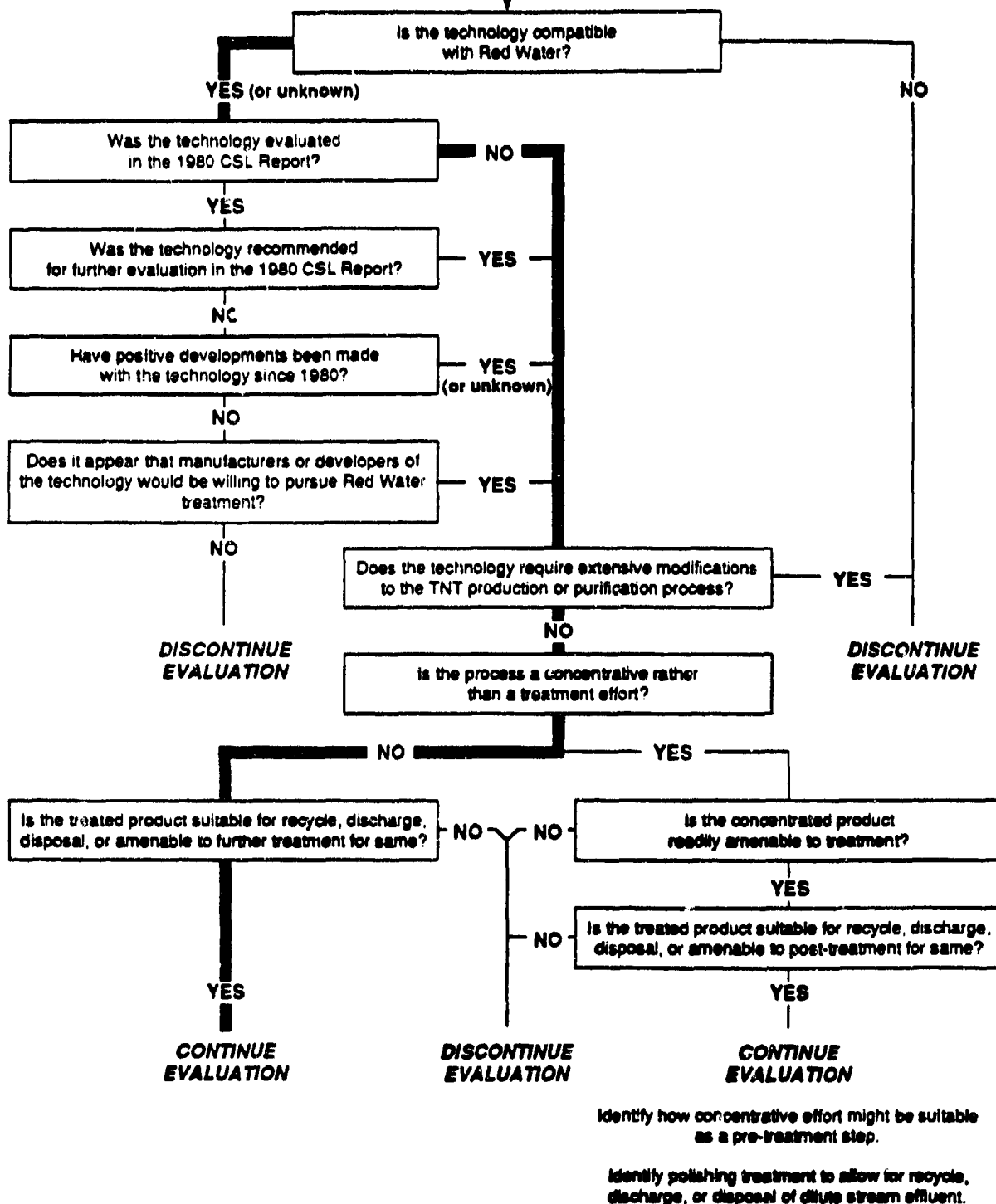


Figure A-3. Prescreening decision tree for biodegradation by white rot fungus on a rotating biological contactor.

COMPOSTING

Composting involves the engineered biological decomposition of a solid waste under controlled conditions and independently of the soil medium. The fact that composting is independent of the soil medium distinguishes this process from land treatment. Composting can be conducted in open piles or in vessels. Composting is usually applied to solids, but can be applied to liquids if a bulking agent such as straw is used to absorb the liquid. To compost a liquid such as red water, the liquid would be sprayed into a soil matrix, which would then be mixed with a bulking agent for aeration and a source of essential nutritional elements. The compost pile must usually be inoculated with a microorganism that can degrade the hazardous waste.

Composting has not been tested on red water based on information available. However, composting was successfully demonstrated in pilot-scale testing to treat high-clay soils that contained mixed wastes consisting of TNT (66%), RDX (25%), HMX (9%), and tetryl (0.3%) with a total concentration of 76,000 ppm (Weston, 1988). The soil was incorporated with manure, straw and alfalfa and then placed in two separate piles under roofs. Blowers were provided to ventilate the piles, using a timer control system below a temperature set point, and feedback control above the temperature set point. The setup also included a drainage trough, sump, and slotted piping.

One pile was maintained at 35°C, and one at 55°C. Moisture was maintained at 50-55 percent. As a result of the fact that the process consumed large amounts of moisture, water had to be added at three separate times over the course of the treatment process. There was no leachate problem. A period of rainfall resulted in water buildup in the sump. An analysis of the rainwater in the sump yielded no detectable concentrations of any explosives. The entire length of treatment was 150 days with significant reduction observed after 80 days. The overall percentage of degradation was 99.9 percent, with final levels of TNT, RDX, and HMX at 3, 45, and 26 mg/kg, respectively. Following the treatment period, low levels of intermediates were

found, including diaminonitrotoluene, 2-amino-4,6-dinitrotoluene, and 4-amino-2,6-dinitrotoluene. Some of these intermediate metabolites may be as hazardous to the environment as the original waste constituents.

Despite the fact that significant overall degradation of the primary contaminants was observed for this mixture, composting has not been demonstrated on red water, which is contaminated with dinitrotoluene sulfonates. Large-scale composting would require that significant amounts of red water be transported to some separate location for distribution into a soil matrix, requiring large amounts of land. Whereas composting warrants consideration for remediation of pre-existing contaminated sites, public concern and associated regulatory issues surrounding the permitting of such a facility for ongoing use would make its implementation extremely difficult, if not altogether impossible.

The prescreening decision tree for composting is shown in Figure A-4 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? No. The toxicity of and high concentration of contaminants in red water could prevent biodegradation in the soil medium. Significant amounts of land would be required for distribution of the red water into a soil matrix.

Composting is not compatible with the characteristics of red water and is not recommended for further evaluation.

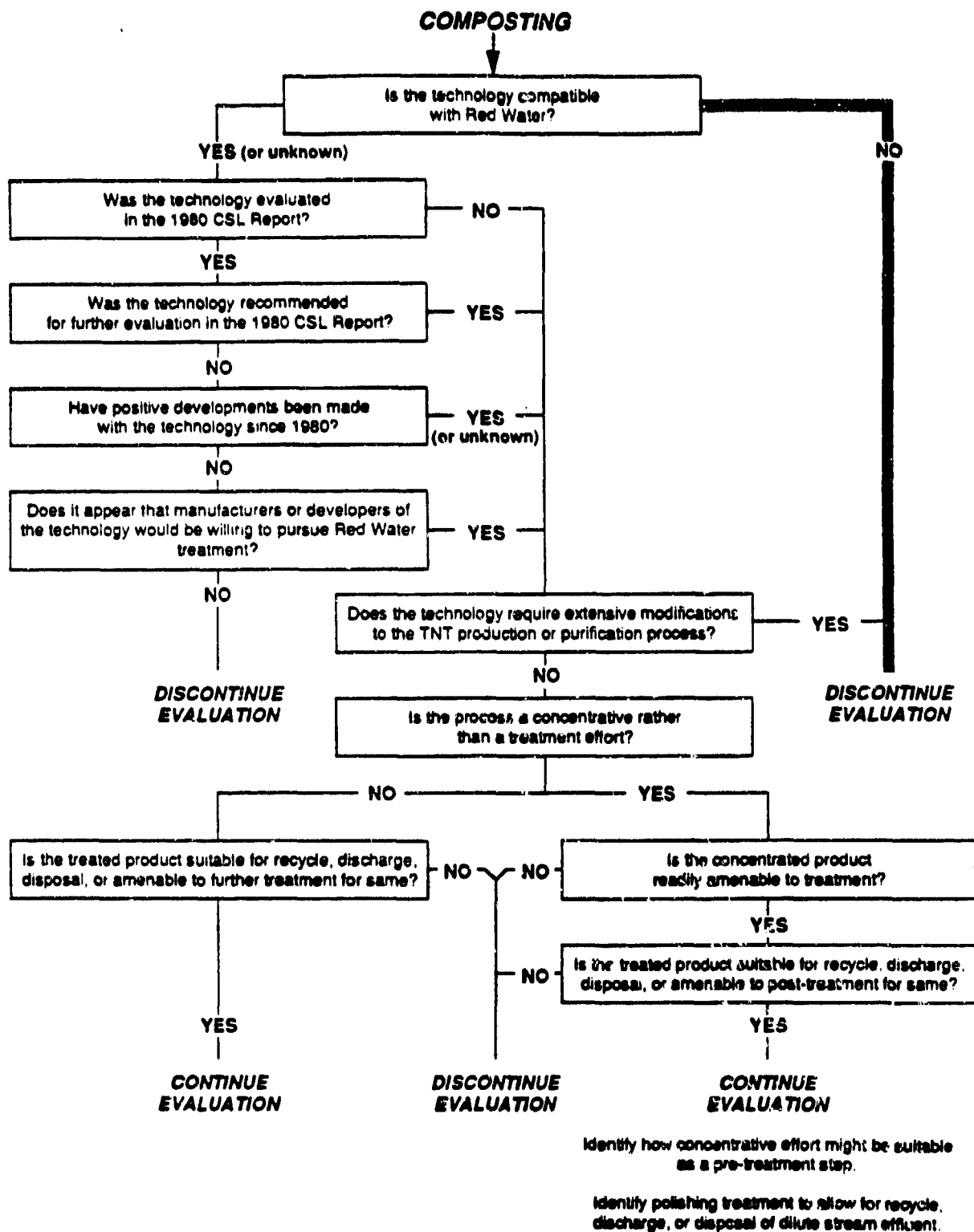


Figure A-4. Prescreening decision tree for composting.

LAND TREATMENT

In land treatment, a waste is mixed with the surface soil so that natural microorganisms present will degrade or immobilize the waste constituents. Wastes must be biodegradable at reasonable rates for land treatment to be a feasible option. In general, the waste should be dilute. Land treatment is generally not considered feasible for radioactive wastes; highly volatile, reactive, or flammable liquids; and inorganic wastes such as heavy metals, acids and bases, cyanides and ammonia. The toxicity and high concentration of contaminants in red water would poison indigenous microbial populations and prevent successful degradation by land treatment.

Land treatment requires large amounts of land and involves spraying or some other means of distribution of wastes into the soil. Public concern and associated regulatory issues surrounding the permitting of such a facility would make implementation of land treatment extremely difficult, if not altogether impossible.

The prescreening decision tree for land treatment is shown in Figure A-5 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? No. The toxicity and high concentration of contaminants in red water would poison indigenous microbial populations and prevent successful degradation by land treatment.

Land treatment is not compatible with the characteristics of red water and is not recommended for further evaluation.



ACIDIFICATION

Acidification was evaluated in the 1980 CSL report. The report contains a thorough process description as well as the results of laboratory tests that have been conducted on this technology.

Acidification is a process whereby the sulfonate group is removed from the 2,4-dinitrotoluene (DNT) sulfonates through acidification of red water. The resulting product, DNT, can then be recycled back into the TNT nitrification process, thereby increasing the yield of TNT. The primary technique for desulfonating the 2,4-DNT sulfonates is thermal hydrolytic desulfonation, which involves heating the DNT sulfonates in an aqueous acid medium. Various acids, temperatures, and pressures have been attempted. Many types of aromatic sulfonic acids have been desulfonated for research and industrial purposes. However, nitroaromatic sulfonic acids resisted desulfonation in studies documented in the 1980 CSL report, and the researchers concluded that this technology was not promising for the treatment of red water.

Acidification received the lowest score of the ten technologies evaluated in the CSL report. A conversation with Everett Gilbert, who was intimately involved in the studies of acidification of red water while at the U.S. Army Armament Research and Development Command (ARRADCOM), revealed that no further studies regarding acidification of red water have been conducted since 1980, and there have been no successful attempts to desulfonate the 2,4-DNT sulfonates in red water (Gilbert 1989).

The prescreening decision tree is shown in Figure B-1 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. Red water has been used in laboratory-scale experiments of acidification. However, some explosions were experienced during these studies, indicating that extreme safety measures would be required.
- ° Was the technology evaluated in the 1980 CSL Report? Yes.

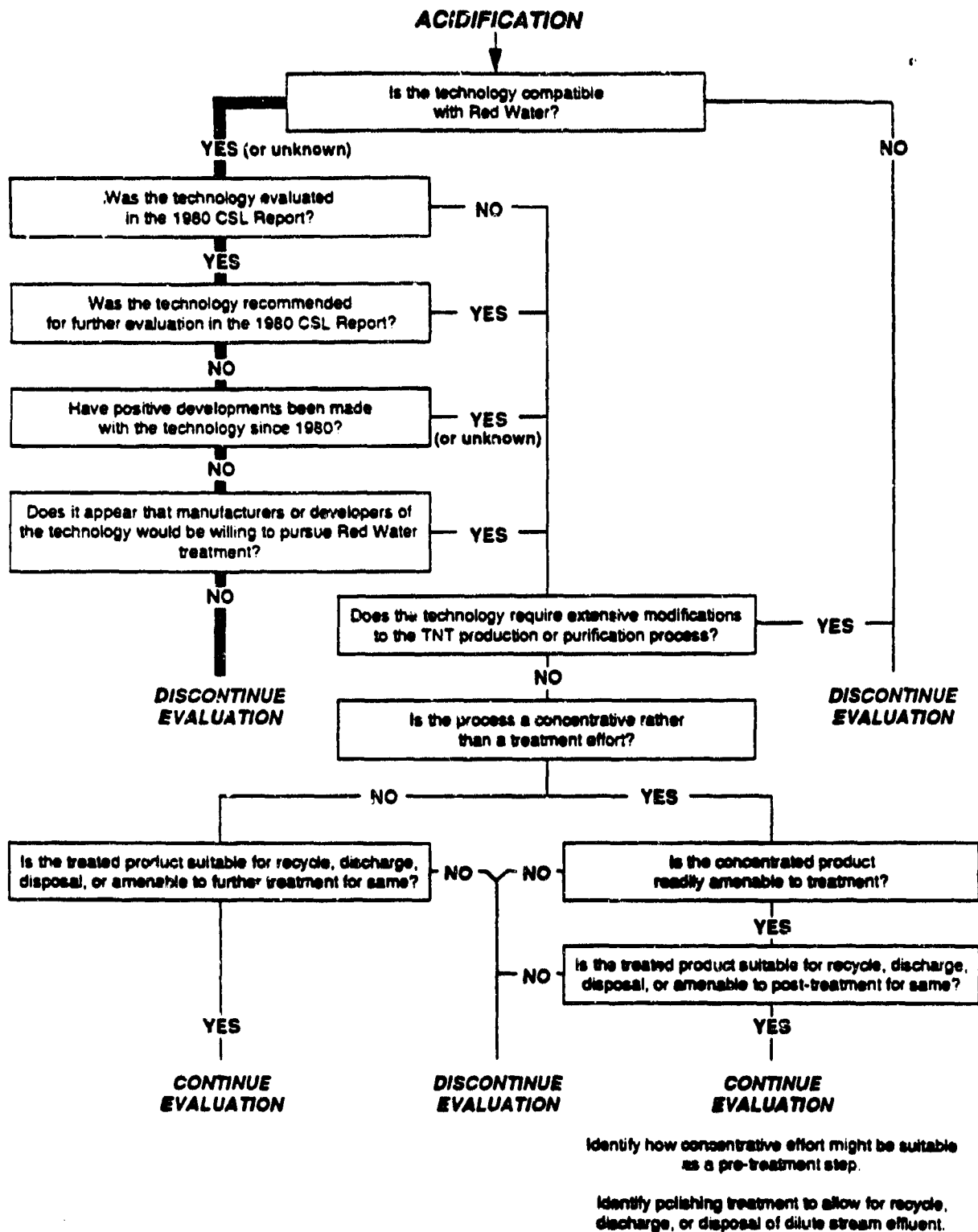


Figure B-1. Prescreening decision tree for acidification.

- ° Was the technology recommended for further evaluation in the 1980 CSL report? No. Acidification received the lowest evaluation of the ten red water disposal methods examined because of disappointing test results, and was not recommended for further evaluation.
- ° Have positive developments been made with the technology since 1980? No. Everett Gilbert indicated that no further studies have been conducted, and none was found in the literature.
- ° Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? No. The technology was not successful at the laboratory scale, and there have been no successful attempts to desulfonate the 2,4-DNT sulfonates in red water. Thus, it is highly unlikely that developers of the technology would be willing to pursue it as a treatment of red water because the treated product is not more suitable for recycle, discharge, disposal, or further treatment than is the original red water.

Acidification is not recommended for further evaluation as a treatment for red water.

CARBON ADSORPTION

Carbon adsorption as a treatment technology involves the removal of constituents from wastewater or air by adherence of the constituents onto carbon particles. The carbon is "activated" to provide a large surface area for adsorption of waste components. This technology is used widely for removing toxic pollutants from aqueous solutions, and has been applied most often to organic compounds, although some inorganics are efficiently adsorbed. Two competing influences that determine whether a compound will be adsorbed are the attraction between solute and carbon surface, and the attraction between solute and solvent. In general, for aqueous solutions, nonpolar compounds with a low solubility in water are most adsorbable on carbon.

Granular activated carbon (GAC) is currently used to treat pink water from Army ammunition plants, but is not used in treating red water. The main contaminant of pink water is 2,4,6-TNT, whereas the main contaminants of red water are dinitrotoluene sulfonate sodium salts. Only trace amounts of 2,4-DNT and 2,4,6-TNT are present in red water. Since DNT and TNT are essentially nonpolar compounds with low solubilities in water, one would expect them to be readily adsorbed by carbon. However, dinitrotoluene sulfonate salts are very soluble in water, which is why the sellite purification process is successful in removing the unwanted TNT isomers from 2,4,6-TNT. Because of this solubility in water, one would not expect these sulfonates to be adsorbed by carbon.

In an early study of using carbon adsorption to treat red water, carbon dosages of 8.34 tons of carbon per million gallons of red water produced only 15.8 to 36.5 percent reduction in organics, while up to 41.7 tons of carbon were required for effective color removal (Schott, 1943.). The researchers concluded that activated carbon treatment was somewhat effective but required excessive amounts of carbon and would be cost prohibitive.

In a more extensive study of carbon treatment of red water from a continuous TNT line, the researchers found that lower pH values increased the adsorption of 2,4,6-TNT (Schulte, 1973). During carbon column studies, efficient TNT removal occurred for pure 2,4,6-TNT in distilled water; however, column treatment of actual red water resulted in very rapid breakthrough of color compounds, although DNT and TNT were efficiently removed. Longer residence times resulted in complete removal of DNT and TNT, but color breakthrough was still rapid. The authors concluded that carbon adsorption was effective in removing DNT and TNT but was not effective in removing the other constituents of actual wastewater.

In a 1987 study, granular activated carbon was used to treat pink water containing DNT, RDX, HMX, and TNT (Hinshaw, 1987). Target effluent criteria of 0.04 mg/L for TNT, 0.03 mg/l for RDX and HMX, and 0.0007 mg/L for DNT were met in the isotherm tests. During pilot-scale multiple-column studies, effluent criteria were met for DNT, RDX, and HMX, but not for TNT. The TNT levels did not decrease significantly beyond the first column, indicating a practical lower limit for TNT reduction under the test conditions. The authors noted that a much higher hydraulic loading rate might achieve the TNT effluent level at the expense of poorer carbon utilization. Carbon adsorption would most likely be less effective in removing the highly polar dinitrotoluene sulfonate salts.

TNT and other nitrocompounds may be removed effectively under some conditions. However, dinitrotoluene sulfonate salts are extremely water-soluble, and are thus unlikely candidates for removal by carbon adsorption. Sulfonates are, in general, very soluble in water; detergents are soluble in water because of the sulfonate end of the detergent molecules. In addition, one researcher writes that the color in red and pink water is due in part to the presence of Meisenheimer complexes that are very difficult to adsorb from water (Rosenblatt, 1972). Additional problems with carbon adsorption would arise from the need to regenerate or dispose of the spent carbon, which would be used up very rapidly because of the high dissolved solids content of red water.

The prescreening decision tree for carbon adsorption is shown in Figure B-2 and the decision tree analysis is provided below.

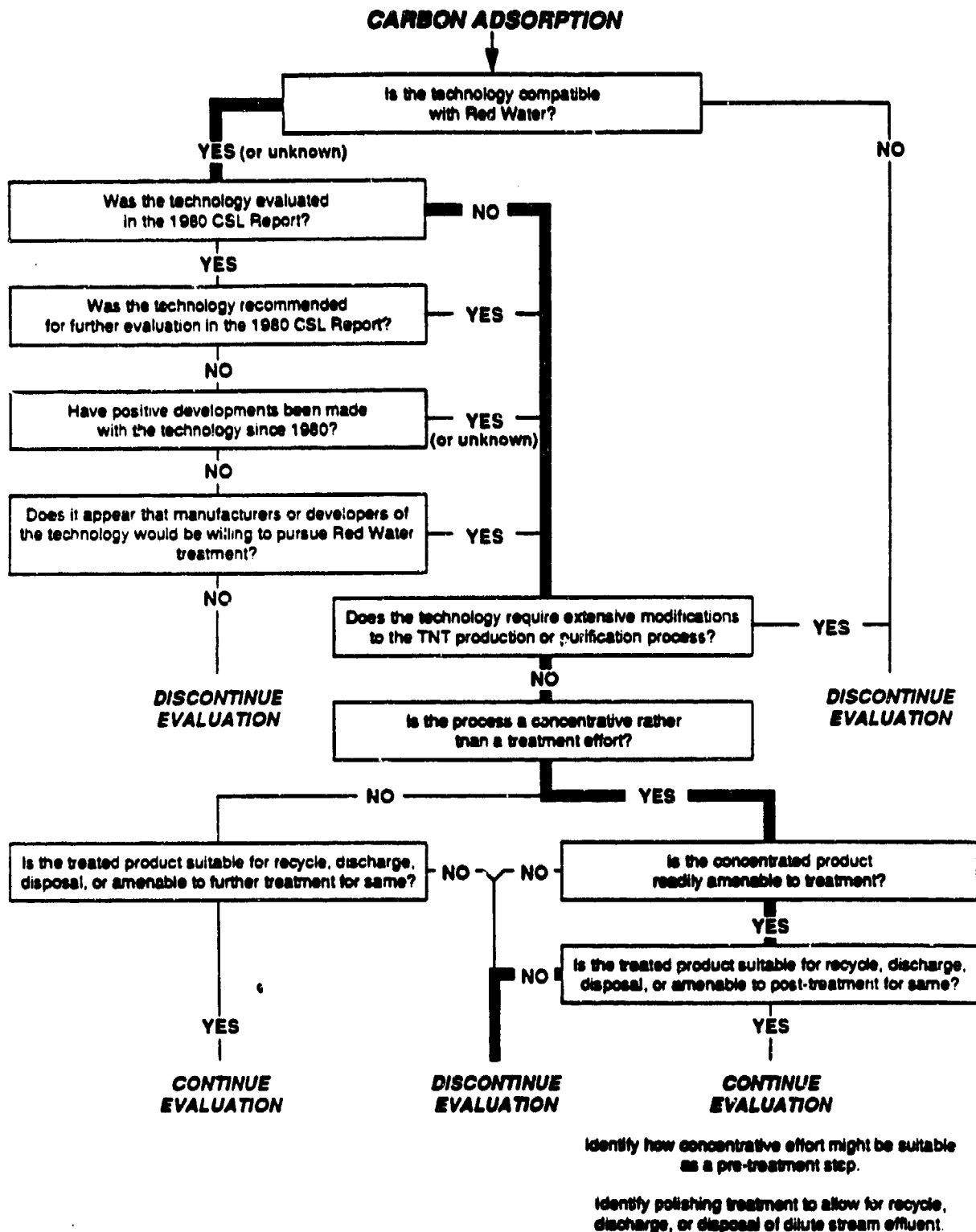


Figure B-2. Prescreening decision tree for carbon adsorption.

- ° Is the technology compatible with red water? Unknown. Carbon adsorption has not been used for the treatment of red water. The concentration of nitroaromatics on the carbon could create a potential for explosion.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No.
- ° Is the process a concentrative rather than a treatment effort? Yes. Carbon adsorption treats the wastewater by concentrating contaminants on the carbon surface. The two products would be spent carbon contaminated with nitroaromatics and other contaminants, and an effluent with a lower concentration of contaminants than red water.
- ° Is the concentrated product readily amenable to treatment? Yes. The spent carbon could potentially be incinerated or thermally regenerated; however, these methods could create air pollution problems as well as a large amount of ash to be disposed.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to post-treatment for same? No. A large amount of ash would require disposal in a landfill. Most importantly, based on poor results of studies conducted to date and the theory behind carbon adsorption, this technology does not appear to be an effective option for the removal of Meisenheimer complexes and dinitrotoluene sulfonate salts from red water. The resulting effluent would probably not meet discharge criteria. Although carbon adsorption is not suited for the treatment of raw red water, it may be useful as a polishing step for the removal of trace DNT and TNT components following treatment by another method.

Carbon adsorption is not recommended for further evaluation.

CATALYZED WET OXIDATION

Catalyzed Wet Oxidation (CWO) is a treatment technology developed by International Technology Corporation (IT) in the 1970s and refined in the early 1980s (Fox, 1988). The process uses a bromide/nitrate-based co-catalyst system in an aqueous solution to effect the oxidation of organics in water or brine.

Conventional wet oxidation processes use heat and pressure to increase the dissolution of oxygen from air into the liquid phase, where the oxygen reacts with dissolved organics in aqueous solution. In CWO, the bromide/nitrate-based catalyst system accelerates the transfer of oxygen to the dissolved state. In this way, very rapid gas and liquid reactions are associated with the catalysts components. Because of the enhanced oxygen transfer, organics can be oxidized at much lower temperatures (165° to 200°C versus 250° to 325°C) and lower pressures than in uncatalyzed wet oxidation. Thus, capital and operating costs, as well as operational problems, are reduced.

Red water treatment using this technology has not been tested. However, a variety of industrial chemicals and certain industrial wastes have been tested on a bench scale and in a one-liter stirred autoclave. Limited data on nitrated aromatics and explosives were encouraging. Dinitroortho secondary butyl phenol was rapidly oxidized by the CWO catalyst system at 200°C with over 90 percent destruction in 15 minutes. A lagoon sediment contaminated with large percentages of TNT, RDX, and tetryl also was tested. Results indicated that at 250°C, 99 percent of TNT was destroyed in 60 minutes, and RDX and tetryl concentrations were reduced to <220 ppm and <75 ppm respectively (matrix effects caused high analytical detection limits). Very preliminary nitrobenzene oxidation data showed a slow destruction rate at 250°C.

If applied to red water, the CWO process would be operated as follows. The wastewater would be acidified; the CWO catalyst components would be added and fed to a CWO reactor system with sufficient residence time to destroy the

nitro bodies. Bench-scale tests would be utilized to optimize the catalyst composition and time/temperature relationships. Red water already has sufficient nitrate for catalytic action; only bromide ion and perhaps a transitional metal ion would be required as added catalyst components.

The reactor system can be designed either as a plug-flow tube reactor or a continuously stirred tank reactor (CSTR). A CSTR offers greater reaction control; however, the feed characteristics and reaction conditions will determine selection of reactor type. For treatment of an organic-rich waste such as red water, the oxidation reaction is expected to occur quite rapidly.

The organic-free effluent from the reactor contains acidic inorganic salts that could be neutralized to precipitate heavy metals. This neutralized solution containing sodium salts of sulfate, nitrate, and bromide can then be subjected to a recovery process that first involves the use of electromembrane technology to generate acids and sodium hydroxide. The acids can then be distilled to recover hydrogen bromide (HBr), leaving a sulfuric/nitric acid mixture that could be recycled for nitric acid recovery.

The decision tree for catalyzed wet oxidation is shown in Figure B-3 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. No testing with red water has been conducted.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water waste stream is treated after it has left the TNT production/purification process.
- ° Is the process a concentrative rather than a treatment effort? No. the process involves destruction of organic contaminants in aqueous solution through oxidation.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. If successful, the effluent would be suitable for discharge. However, the by-products resulting from red water treatment using the CWO process are unknown at this time.

The Catalyzed Wet Oxidation process has survived the prescreening decision process. Prior to further evaluation of this technology, additional information is needed regarding the application of this process to red water treatment and the composition of by-products generated by the CWO process.

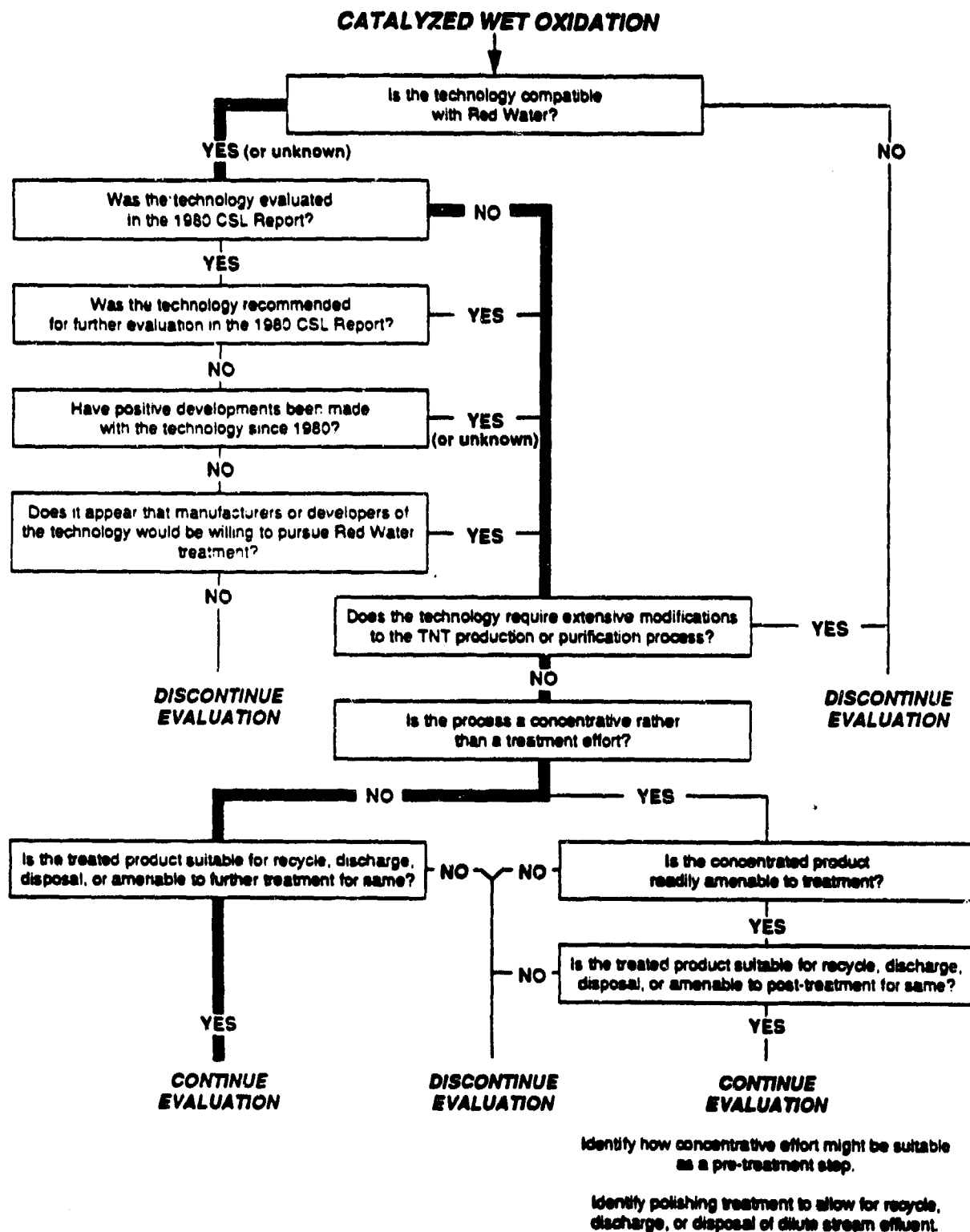


Figure B-3. Prescreening decision tree for catalyzed wet oxidation.

FREEZE TECHNOLOGY

When the temperature of a solution is dropped until freezing occurs, the ice crystals that form are pure water, with the dissolved material being concentrated in the liquid phase. The separation is close to but not exactly complete because: 1) some solids can be trapped in the ice crystals, and 2) solution adhering to the ice crystals must be removed by washing in the final step of a concentration process. Commercially, freeze concentration is used to concentrate heat sensitive solutions; for example, coffee extract is freeze concentrated prior to freeze drying to minimize flavor loss. Because of the refrigeration equipment required, freeze concentration has high capital and operating costs compared with other concentration technologies. At one time, freeze concentration was investigated by the Office of Saline Water as a means of water desalination, but it was found to be uneconomical.

A research project sponsored by the U.S. Army Armament Research and Development Command (ARRADCOM) reported the results of 0.17 to 0.68 gallons per minute scale testing of concentrating red water by freezing (Duvall, 1979). The concept was that only water as ice would be removed from the system, resulting in a more concentrated red water stream. In a system with two stages of freezing, red water concentrations of 24 percent were obtained with the removed water having less than 100 ppm total dissolved solids (TDS). In two tests, brine concentration reached 36 percent with TDS of the "clean" water product being 700 to 1,400 ppm. The report indicates that approximately 35 percent concentration can be achieved through standard evaporation. The authors predicted that this concentration could also be achieved through freezing. Concentration is hindered by dissolved solids precipitation with the initial precipitate being Glaubers Salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The report concluded that freeze technology is not applicable to red water treatment.

If concentrating red water would be advantageous, a stirred tank evaporator would probably be cheaper to build and operate than a freeze

concentration system. Also, the condensate from evaporation would be as clean or cleaner than the effluent from a freeze concentrator. Evaporators are in commercial operation that concentrate salt solutions to a slurry. Agitation is used to keep the crystallized salt in suspension in the evaporator so the heat transfer surfaces are not fouled. When the concentrated material is discharged the salt is removed and washed in a centrifuge.

However, with red water, if a dilute fraction with 100 ppm TDS and a concentrated fraction with about 220,000 ppm TDS are obtained and the total volume is unchanged, then the advantages are minimal since both fractions still need treatment.

A search of Chemical Abstracts found no indication of technological advances since the 1979 report. Jim Carrazza of ARDEC was unaware of any advances.

The prescreening decision tree for freeze technology is shown in Figure B-4 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. All of the material in red water must still be treated. There is no advantage using freeze technology unless either water is obtained that can be discharged with minimal treatment or the two fractions are more amenable to treatment than the original red water.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. Freeze technology would be applied to the red water effluent from the process.
- ° Is the process a concentrative rather than a treatment effort? Yes. A concentrated and a dilute stream would be produced.
- ° Is the concentrated product readily amenable to treatment? No. Freeze concentration would produce a concentrated and a dilute stream, both of which would require further treatment. The final result is not necessarily more amenable to treatment than red water.

On this basis, freeze technology for red water treatment is not recommended for further evaluation. If concentration is useful, evaporation would be much cheaper and produce a cleaner separation.

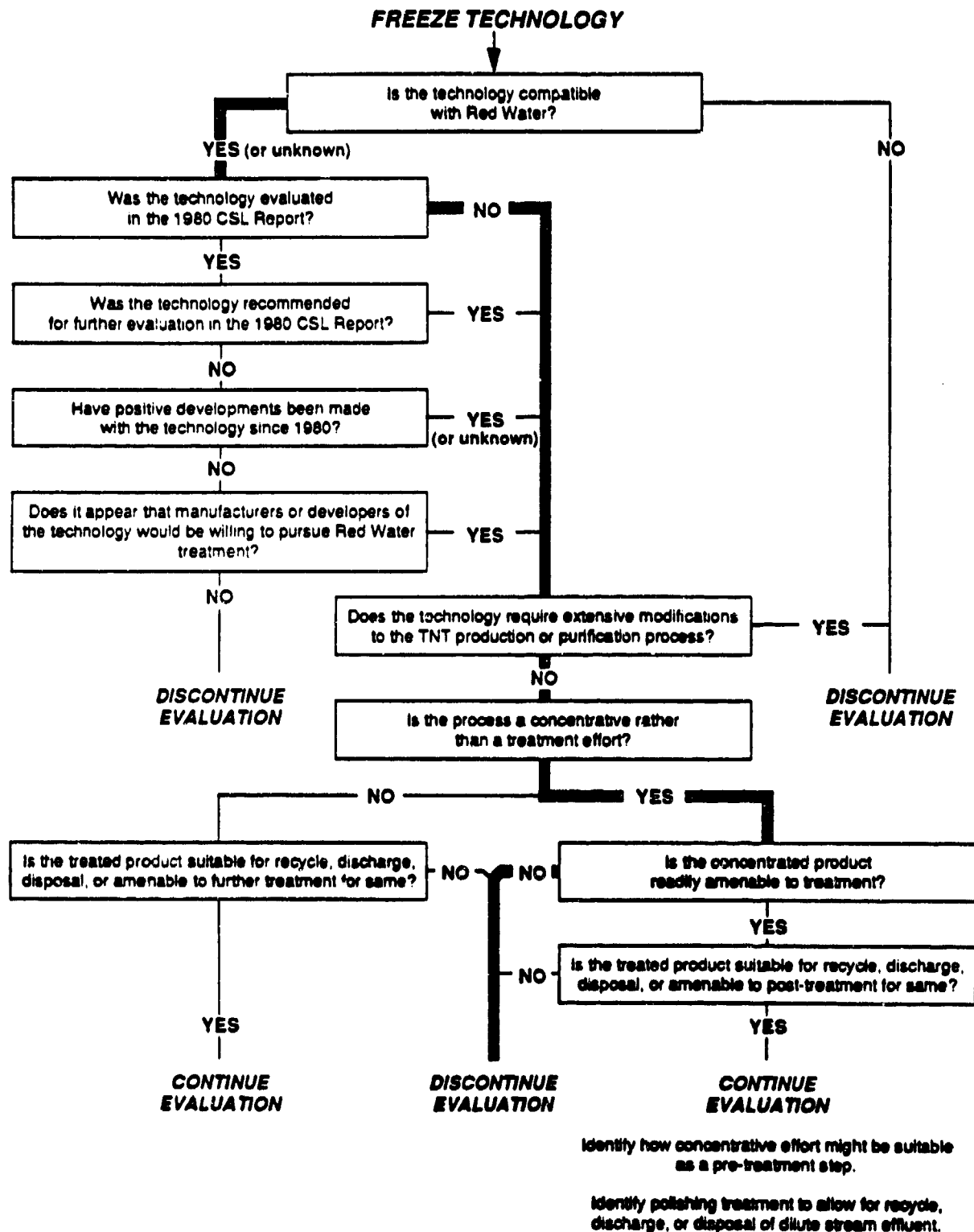


Figure B-4. Prescreening decision tree for freeze technology.

ION EXCHANGE

Ion exchange is a technology for removing low concentrations of selected ions from a wastewater stream. Ion exchange resins are available that will remove either cations or anions.

To understand how an ion exchange resin works, a water softener will be used as an example. A water softener contains a resin that has an affinity for cations. At the beginning of a treatment cycle, the active sites on the resin are occupied by sodium ions. As water flows through the resin, calcium and magnesium, which will bind tighter to the resin than sodium, displace the sodium and are removed from the water. The sodium in turn takes the place of these calcium and magnesium ions in the water. The resin bed is considered saturated when all the active sites have been replaced with calcium and magnesium ions.

When the bed is finally saturated, magnesium and calcium ions will be detected in the effluent from the bed. At this point, the bed must be regenerated. The regeneration has three steps: first the bed is drained, then a concentrated solution of sodium ions is introduced into the bed in the form of brine, and finally, the bed is drained and washed to remove the regeneration solution. The principle behind regeneration is that the high concentration of sodium ions will overwhelm and displace the calcium and magnesium ions attached to the resin.

Ion exchange is only practical for removing contaminants that are present in wastewater at a low level, typically 1000 ppm or less. The higher the concentration of material to be removed in the feed stream, the faster the ion exchange resin will become saturated and have to be regenerated. During regeneration, the compound that was removed is rediluted in the regeneration water, and the amount of the regeneration solution is constant for a given column size and application.

Ion exchange resins are generally described in terms of bed volume (BV), where a BV is the actual volume of the bed. Resin regeneration typically requires three BV of the regenerating material and the following rinsing operation requires 3.5 to 13.5 BVs (Albright et al., p. 352). Assuming that 6 BVs can be used to rinse the bed, a total of 9 BVs of regeneration and wash water will be produced each time the resin is regenerated.

As shown in the attached calculation, red water contains about 2.36 equivalents per liter. The reference cited earlier lists 10 resins and gives their ion-holding capacity (Albright et al., p. 384). These capacities range from 0.56 equivalents per liter to 2.75 equivalent per liter of resin. The 2.36 equivalents per liter in red water would be half cations and half anions, or 1.18 equivalents of cations and 1.18 equivalents of anions per liter. Assuming the highest capacity bed could be used, the 2.75 equivalents per liter resin would be saturated with 2.3 liters of red water. The resin would then have to be regenerated, and this regeneration would produce about 9 liters of regeneration and wash water that contained the contaminants that were originally removed. The net result is that the contaminants in 2.3 liters of red water would be transferred to 9 liters of regeneration and wash water. In addition, at the point at which the resin is saturated, the resin contains red water that has not been treated since all the active sites have been used. This untreated red water would also wash back in the regeneration water.

Ion exchange could possibly be used to remove the heavy metals. These metals are present in concentrations well below 1000 mg per liter, and resins can be found that preferentially pick up certain metal ions over other ions. If this application were used, the red water would have to be filtered to remove suspended solids. The ion exchange bed will act as a filter itself and, if fed with suspended solids, they tend to plug the bed.

In another, completely different application of ion exchange, an ion exchange bed or column can be used to effect separations of a mixture into its components. This has been applied to obtain clean separations of the lanthanide rare earths. However, this technology has been applied to the

production of products having values of dollars per fraction and is not applicable to wastewater treatment.

The prescreening decision tree for ion exchange is shown in Figure B-5 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? No. The 15 percent total dissolved solids (TDS) far exceeds the concentration that can be processed by ion exchange. Michael Adams of Rohm & Haas said that 15 percent TDS was too concentrated to apply ion exchange technology and that 1000 ppm or less was more typical (Adams, 1989). The high concentration material will actually produce more contaminated water than will be cleaned up due to the volumes of regeneration and wash water that must be used once the bed becomes saturated.

Ion exchange technology is not applicable to the concentrated solutions found in red water and, as such, is not recommended for further evaluation.

CLIENT U.S. Army
LOCATION Radford, Virginia
SUBJECT Equivalence in Red Water



PN 3769-2-C Sheet No 1
Checked By WEG Date 3/14/89
Computed By JES Date 2/20/89

Estimation of the number of equivalents in red water is as follows:

Density = 1.1
Solids content = 15 percent

One liter of red water contains:

$$\frac{1.1}{1} \times \frac{1,000 \text{ gm}}{1} \times 1.1 \times 0.15 \text{ gms solids} = 165 \text{ gms solids}$$

The equivalents of the major components are calculated as follows:

- A) Na_2SO_4 and NaHSO_4 are 32.3 percent of the solids. Calculate as all Na_2SO_4

$$\frac{165 \text{ gms}}{\text{gm}} \times \frac{0.323 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{142 \text{ gm}} \times \frac{3 \text{ eq}}{\text{mole}} = 1.13 \text{ eq/l}$$

- B) NaNO_2 is 11.2 percent of the solids

$$\frac{165 \text{ gms}}{\text{gm}} \times \frac{0.112 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{42 \text{ gm}} \times \frac{2 \text{ eq}}{\text{mole}} = 0.536 \text{ eq/l}$$

- C) NaNO_3 is 1.5 percent of the solids

$$\frac{165 \text{ gms}}{\text{gm}} \times \frac{0.015 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{85 \text{ gm}} \times \frac{2 \text{ eq}}{\text{mole}} = 0.058 \text{ eq/l}$$

- D) Calculate the organics as sodium dinitrotoluenesulfonate, MW = 284

$$\frac{165 \text{ gms}}{\text{gm}} \times \frac{0.55 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{284 \text{ gm}} \times \frac{2 \text{ eq}}{\text{mole}} = 0.639 \text{ eq/l}$$

$$\text{Total eq per l} = 1.13 + 0.536 + 0.058 + 0.639 = 2.36 \text{ eq/l}$$

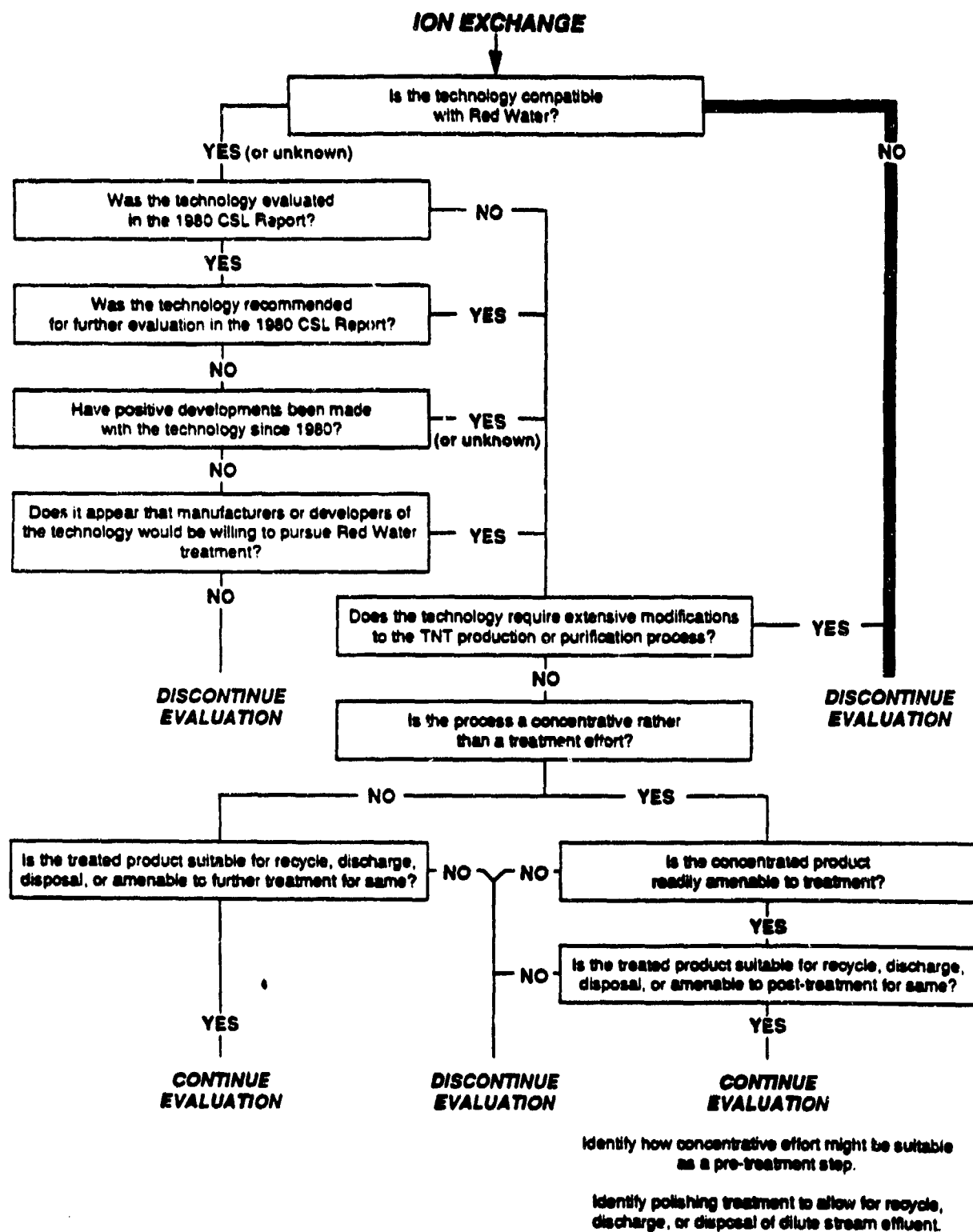


Figure B-5. Prescreening decision tree for ion exchange.

LIQUID-PHASE OXIDATION

In liquid-phase oxidation, strong oxidizing agents (ozone, hydrogen peroxide, or calcium hypochlorite) are used to convert wastes to nonhazardous substances such as carbon dioxide and water. Ultraviolet light or ultrasound are sometimes used in conjunction with these oxidants to increase the rate of reaction.

These oxidizing agents have been used to oxidize aqueous solutions of TNT (trinitrotoluene) to carbon dioxide and water. TNT concentrations were of the order of 100 milligrams per liter (corresponding to those found in pink water) and the effectiveness of the oxidizing agents (ozone and hydrogen peroxide) was enhanced with ultraviolet light or ultrasound. None of the studies traced or mentioned the fate of chemically bound nitrogen. These possibly could have been converted to nitrogen oxides and emitted as such. Table B-1 presents a summary of this work and the sources of information.

All of the previous work was intended to develop methods of treating pink water, which consists chiefly of dissolved TNT. None of the workers applied the technology to red water, which contains dinitrotoluene sulfonate salts, or to solutions containing similar types and quantities of dissolved solids. The oxidizability of the components in red water is unknown. The fate of chemically combined nitrogen such as nitrates, nitrites, and organic nitro groups during chemical oxidation has not been established. There may be significant nitrogen oxide emissions.

The prescreening decision tree for liquid-phase oxidation is shown in Figure B-6 and the decision tree analysis is provided below:

- Is the technology compatible with red water? Unknown. The technology has not been tested on red water.
- Was the technology evaluated in the 1980 CSL report? No.
- Does the technology require modifications to the TNT production or purification process? No. Waste streams are treated after they have left the process.

TABLE B-1. SUMMARY OF RESULTS OBTAINED BY THE LIQUID PHASE OXIDATION OF TNT SOLUTIONS

Treatment	Scale of work	Method treated	Results
Ozone and ultraviolet light (Fochtman and Hoff, 1975), IIT Research Institute	Four liter reactor	Synthetic pink water with 100 mg/liter of TNT and 2 g/liter of total solids	Total organic carbon (TOC) was reduced from 60 mg/l to 18 mg/l. The reaction stopped after two hours. Twelve pounds of ozone were required to oxidize one pound of TOC.
Ozone and ultraviolet light (Burrows, 1983), U.S. Army Bio-engineering R&D Lab, Fort Detrick, Maryland	6 liters/minute	TNT levels, about 100 mg/liter	Ultraviolet light and ozone destroys TNT in solution. It may be "suitable for removal of TNT from small process streams" (about 20,000 gallons per day according to Burrows).
Ozone and ultrasound (Slenska, 1985), University of Arizona	0.45 cc and one liter reactor	Synthetic TNT and RDX solutions, 70 mg/liter of TNT, 30 mg/liter of RDX	Achieved 99 percent destruction of TNT in 60 minutes, required 67 pounds of ozone per pound of TNT.
Hydrogen peroxide and ultraviolet light (Andrews, 1965), Naval Weapons Support Center, Crane, Indiana	10 gallons per minute	Synthetic and actual pink water	Total organic carbon was reduced from 30 to 40 ppm to between five and eight ppm.
Calcium hypochlorite (Ca(ClO) ₂), (Semenov, et al, 1965), University of Minnesota	Pilot plant scale	TNT from cleaning and dismantling of shells	Requires a 10 to 1 weight ratio of calcium hypochlorite to TNT. TNT destruction was essentially complete.

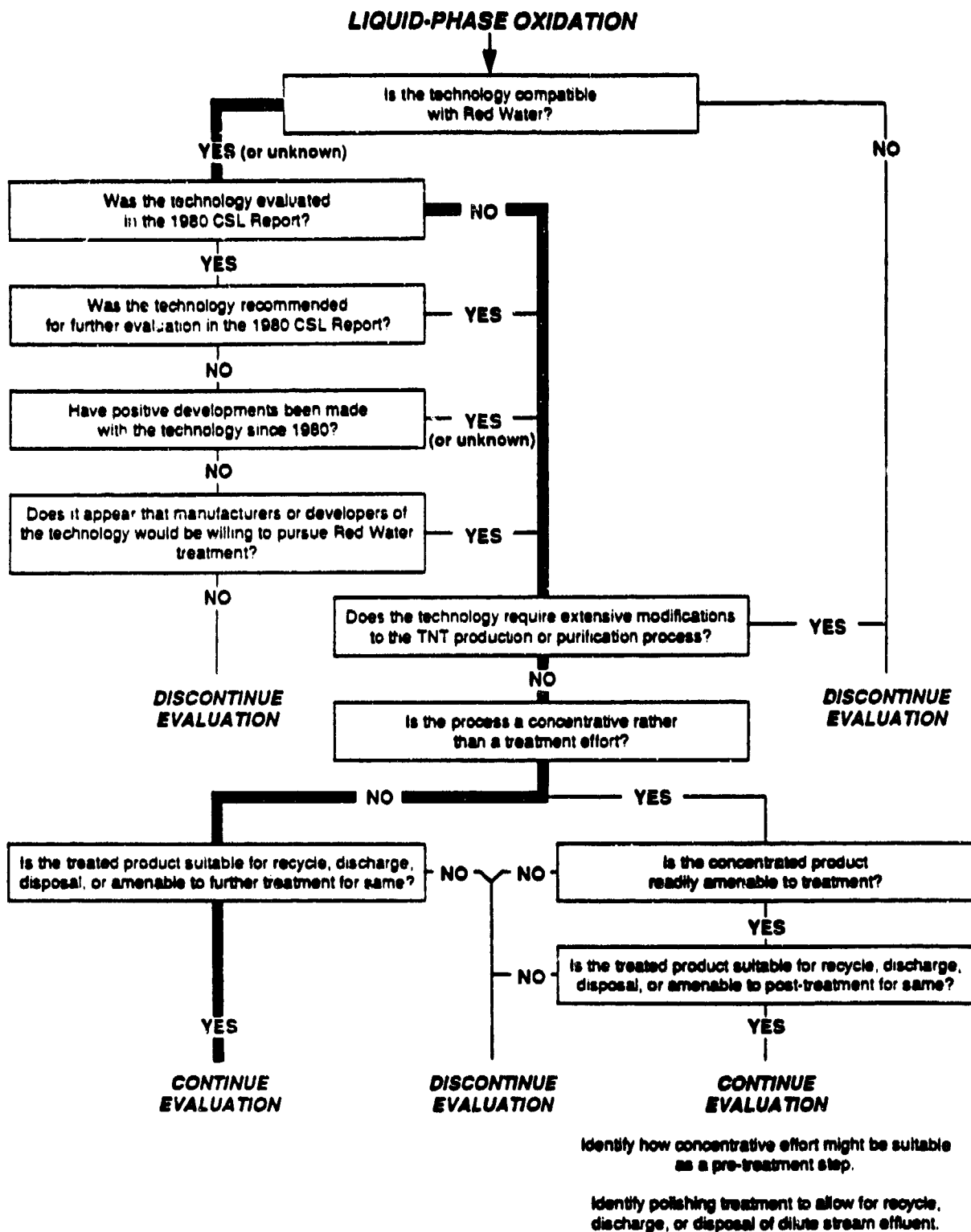


Figure B-6. Prescreening decision tree for liquid-phase oxidation.

- Is the process a concentrative effort? No. If successful, the organic carbon and hydrogen would be oxidized to carbon dioxide and water.
- Is the treated product suitable for recycle, discharge or disposal, or amenable to further treatment for the same? Yes. If successful, the product would be suitable for discharge. The fates of chemically bound nitrogen, the oxidizability of dinitrotoluene sulfonates, and the oxidizability of inorganic nitrites and sulfites have not been established. The previous work on pink water would be of little value and extensive work would be required.

This technology has survived the go/no-go decision tree analysis, due more to a lack of information than to positive indication that the technology is practicable. The process might be useful as a polishing treatment downstream of a technology that removed most of the contaminants.

REVERSE OSMOSIS

Osmosis results from the properties of a semi-permeable membrane. The membrane is a barrier through which solvent molecules can pass but dissolved material or solute cannot pass. The membrane must have pores large enough to allow solvent molecules to pass through but too small to allow solute molecules to pass.

Assume that on one side of a semipermeable membrane there is a solution and on the other side of the membrane there is a more dilute solution, or pure solvent. By the principles of osmosis, the solvent molecules will pass through the membrane from the dilute solution to the concentrated solution to equalize the solvent concentration on each side of the membrane. The driving force behind the passage of solvent molecules through the membrane is the osmotic pressure. The passage of solvent molecules through the membrane can be halted by imposing upon the more concentrated solution a pressure just equal to the osmotic pressure. If the imposed pressure exceeds the osmotic pressure, then solvent molecules will pass through the membrane from the more concentrated solution to the dilute solution or pure solvent. This is opposite to the direction of spontaneous flow and is the principle of reverse osmosis (RO).

The pressure required to cause this reversal of flow is dependent on the concentration of ionic and nonionic material in the solvent. Using an equation that approximates this pressure, the calculated osmotic pressure for red water is 774 pounds per square inch (psi) (see attached calculations). The actual pressure would have to be determined experimentally. As reverse osmosis took place, the red water solution would become more concentrated and the osmotic pressure would increase. Thus, further concentration through reverse osmosis would require still higher pressure. Lynn Applegate of DuPont published a review article on reverse osmosis in the June 11, 1984, issue of Chemical Engineering that indicated the upper pressure limits for a

reverse osmosis membrane was 1,000 psi (Applegate, 1984). David Warner of DuPont in a telephone conversation said that the limit had been extended to 1,200 psi (Warner, 1989). Applegate wrote that the working pressure of the system needed to be about 200 psi greater than the osmotic pressure. Hence, using RO to concentrate red water would quickly reach the pressure limit of the membrane as the concentration increased. Applegate pointed out that reverse osmosis is usually not applicable for concentrated solutions.

Reverse osmosis does not produce pure water. Applegate sites examples where potable water with 500 milligrams per liter (mg/l) of total dissolved salts (TDS) is produced from sea water having 42,000 mg/l of TDS and a Key West, Florida plant where water having 375 mg/l of TDS is obtained from 38,000 mg/l of TDS. Warner indicated that 300 mg/l of TDS is about the lowest concentration that can be obtained. For sea water, these results are very satisfactory, but for red water, the water passing through the membrane would have TDS concentrations comparable to pink water and would need treating since unacceptable levels of nitrocompounds would probably still be present. Organic TDS would have to be at or near zero mg/l. The actual results would probably be two or more fractions that would still have to be treated and with a net increase in volume when membrane washings were included.

The equation for calculating osmotic pressure is identical to the ideal gas equation except that the constant is slightly different: 0.0815 liter-atmospheres per degree per mole for osmosis and 0.0821 for an ideal gas. "N" is the moles per liter of particles. For non-ionized molecule such as sugar, moles of particles and of molecules are the same. For ionized molecules, moles of particles are greater than of molecules; double for sodium nitrate, sodium nitrite, and sodium nitrotoluene sulfonates, and triple for sodium sulfate and sodium sulfite. Calculations of the theoretical osmotic pressure of Radford Army Ammunition plant red water are attached.

The prescreening decision tree for reverse osmosis is shown in Figure B-7 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown, but likely. Applegate states that for industrial wastes, a pretreatment program would need to be developed through pilot plant testing. The program would include removal of colloidal solids through coagulation and

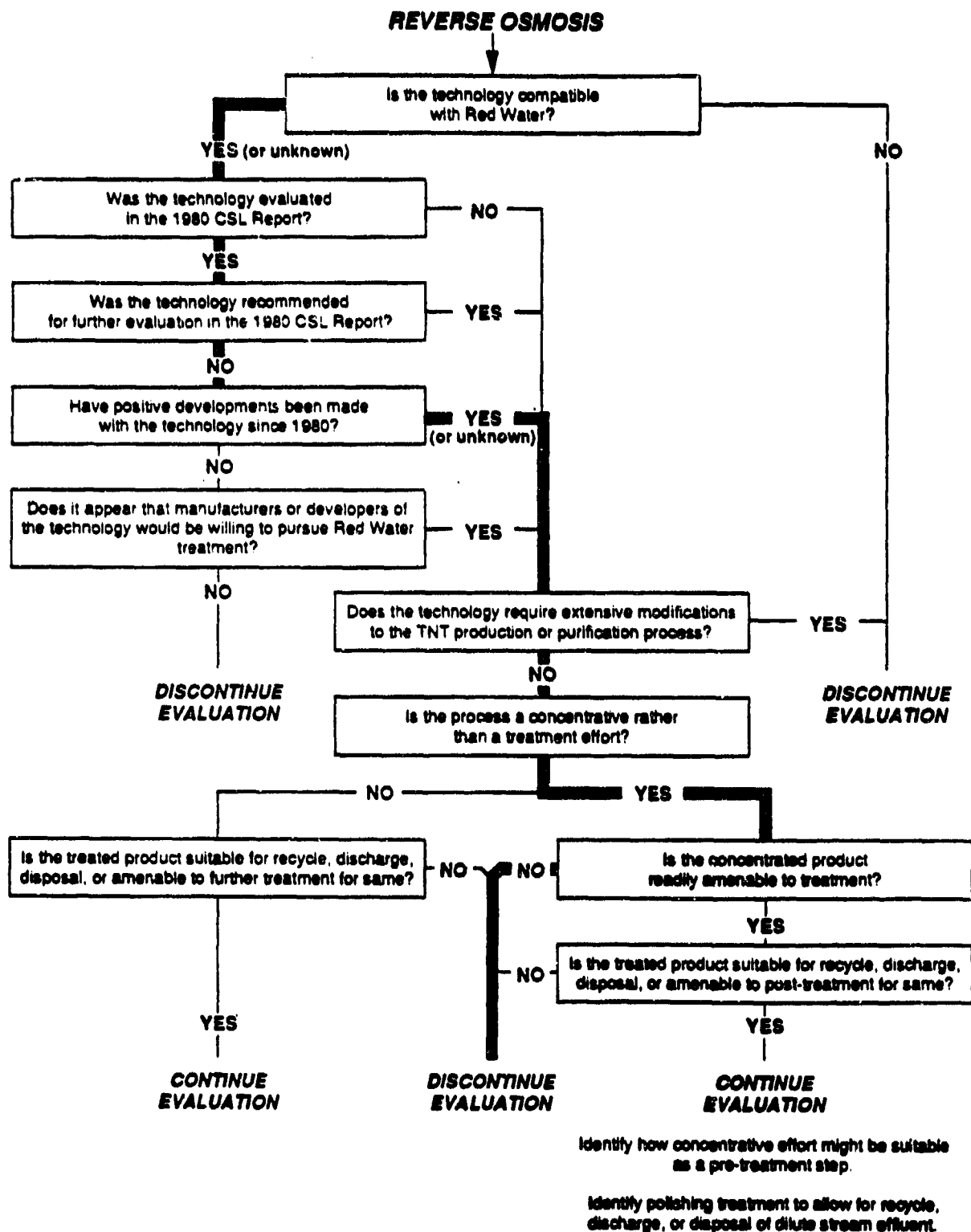


Figure B-7. Prescreening decision tree for reverse osmosis.

filtration and the removal of suspended solids through filtration. These solids would also be toxic wastes and would require treatment. Toxicity would be due to the nature of the solids and/or entrained red water since such solids are typically 90 or more percent water on an apparent dry solids basis. The long-term susceptibility of the membrane to red water would have to be established. This would determine the choice of membrane.

- ° Was the technology evaluated in the 1980 CSL report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? No. Reverse osmosis was ranked ninth of the ten technologies evaluated.
- ° Have positive developments been made with the technology since 1980? Yes, but probably insufficient to warrant reevaluation. Pressure limitations had been extended from 1,000 to 1,200 psi so that the product water could have TDS of at least 300 mg/l. However, reverse osmosis is usually not applicable for solutions more concentrated than sea water. Red water has dissolved solids of 165 grams per liter while sea water has about 37 grams per liter.
- ° Does the technology require extensive modifications to the TNT production or purification process? No.
- ° Is the process a concentrative rather than a treatment effort? Yes. The red water would be concentrated, and an additional water stream would be created with a total dissolved solid concentration greater than 300 mg/l. However, if red water concentration were an objective, evaporation would be a viable alternative with respect to cost, technology status, and production of a condensate that could be discarded with little or no additional treatment.
- ° Is the concentrated product readily amenable to treatment? No. The end result is not necessarily a significant improvement over the original waste stream. The best anticipated success would be to remove half of the water, leaving a concentrated residue that would still have to be treated and a dilute effluent that would also require treatment. The total volume to be treated would actually be increased from washing and cleaning the membrane. A major R&D effort would be required to achieve modest gains.

Reverse osmosis is not recommended for further evaluation.

CLIENT U.S. ArmyLOCATION Radford, VirginiaSUBJECT Osmotic Pressure of Radford
Army Ammunition Plant Red WaterPN 3769-2-C Sheet No. 1Checked By WEG Date 3/14/89Computed By JES Date 2/20/89

From analysis, red water has a specific gravity of 1.1 and is 15 percent solids.

The osmotic pressure of an ideal solution is given by the following equation:

$$P = 1.12 (T + 273) \Sigma m_i$$

where: P = pressure, psi

T = Temperature, °C

Σm_i = Summation of molalities of all ionic and nonionic constituents in the solution

This equation is from "Chemical Engineering", June 11, 1984, p. 65.

A copy of an analysis of the solids in red water is attached. The total molality is estimated as follows:

The total grams of solids in 1 l is:

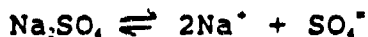
$$\frac{1 \text{ l}}{1} \times \frac{1100 \text{ gms}}{1} \times \frac{0.15 \text{ gms solids}}{\text{gm}} = 165 \text{ gm solids}$$

Using the analysis of red water solids the total moles of dissolved solids is calculated:

A) Na_2SO_4 and Na_2SO_3 are 32.3 percent of the solids.

Calculate these as all Na_2SO_4

$$\frac{165 \text{ gm}}{1} \times \frac{0.323 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{142 \text{ gms}} = 0.375 \text{ moles/l}$$



the number of moles of ions is $3 \times 0.375 = 1.13 \text{ moles}$

B) NaNO_2

$$\frac{165 \text{ gm}}{1} \times \frac{0.112 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{69 \text{ gms}} = 0.268 \text{ moles/l}$$



CLIENT U.S. Army

LOCATION Radford, Virginia

SUBJECT Osmotic Pressure of Radford
Army Ammunition Plant Red Water



PN 3769-2-C Sheet No. 1

Checked By WEG Date 3/14/89

Computed By JES Date 2/20/89

C) NaNO_3

$$\frac{165 \text{ gm}}{1} \times \frac{0.015 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{85 \text{ gms}} = 0.029 \text{ moles/l}$$

$$0.029 \times 2 = \underline{0.058 \text{ moles}}$$

D) Calculate all the nitro bodies as sodium dinitrotoluenesulfonate, $\text{C}_6\text{H}_4\text{N}_2\text{O}_6\text{SNa}$
= 284

$$\frac{165 \text{ gm}}{1} \times \frac{0.055 \text{ gm}}{\text{gm}} \times \frac{\text{mole}}{284 \text{ gms}} = 0.320 \text{ moles/l}$$

Assume a factor of 2 to convert to the moles of ions:

$$0.320 \times 2 = \underline{0.639 \text{ moles}}$$

The total moles/l of ions is thus:

$$1.13 + 0.536 + 0.058 + 0.639 = 2.36 \frac{\text{moles ions}}{1}$$

The osmotic pressure at 20 °C is thus:

$$P = 1.2 (20 + 273) (2.36) = 774 \text{ psi}$$

STABILIZATION/SOLIDIFICATION

Stabilization and solidification both refer to treatment processes that are designed to accomplish one or more of the following results: 1) improve the handling and physical characteristics of the waste; 2) decrease the surface area of the waste mass across which transfer or loss of contaminants can occur; and/or 3) limit the solubility of any hazardous constituents of the waste.

Stabilization techniques are generally those whose beneficial action is primarily through limiting the solubility of contaminants with or without change or improvement in the physical characteristics of the waste. Stabilization systems attempt to reduce the solubility or chemical reactivity of a waste by changing its chemical state or by physical entrapment. Stabilization usually involves adding materials that ensure that the hazardous constituents of a waste are maintained in their least mobile or toxic form.

Solidification implies that the beneficial results of treatment are obtained primarily, but not necessarily exclusively, through the production of a solid block of waste material having a high structural integrity. Solidification systems attempt to convert the waste into an easily handled solid with reduced hazards from volatilization, leaching, or spillage.

Stabilization/solidification techniques have been evaluated by S-CUBED on synthetic sludges that simulated some types of military waste sludge. Two types of waste were analyzed: inorganic-contaminated waste containing lead, cadmium, and chromium, and organic-contaminated waste containing nitrocellulose. Nitrocellulose is used to provide mechanical strength as well as readily available energy to gun and rocket propellants. It is found in sludge from the Nitroglycerin-1/Alcohol Rectification operations at the Radford facility.

The wastes were analyzed in aqueous and dewatered states. Polysilicate fixatives mixed with Portland cement and fly ash were applied to the aqueous

inorganic waste. Polysilicates were applied to the aqueous organic waste. Polysulfides and amine-cured epoxides were applied to the dewatered inorganic and organic wastes, respectively. The polysulfide fixative successfully isolated the heavy metals and the amine-cured epoxides successfully fixed the nitrocellulose-containing sludges.

S-CUSED also evaluated commercial non-ionic resins for their ability to remove nitrocompounds normally present in pink water and sludges derived from it. Pink water is the washings produced in the manufacturing and loading plants and contains dissolved TNT and dinitrotoluene. These nitrocompounds represent only a trace amount of the solids in red water.

The non-ionic resins were shown to effectively remove TNT from the synthetic waste solution. In addition, there appeared to be potential formation of a reaction product between TNT and the resin, possibly resulting in the stabilization of the waste. Even though the solution was synthetic and simulated pink water, in contrast to red water, the stabilization of the explosive constituents of the waste is a potentially significant finding. Red water is classified as a hazardous waste because of its reactivity.

It must be noted, however, that no experimental work has been performed on red water or solutions containing very similar types and quantities of dissolved solids. No experimentation has been performed that shows that stabilization/solidification will render red water non-reactive, which is a criterion which must be met before land disposal is permitted.

A conversation with Jesse Connor of Chemical Waste Management, a hazardous waste management firm, confirmed that there have not been any attempts at stabilization/solidification of red water. Mr. Connor stated that the red water could most probably be treated successfully with stabilization/solidification techniques but that, because of current regulations requiring no land disposal due to reactivity, the organic nitrocompounds would have to be destroyed by incineration or some chemical treatment process such as controlled oxidation due to their explosive nature. The stabilization/solidification process would result in containment, not destruction of the reactive nitrocompounds.

The prescreening decision tree for stabilization/solidification is shown in Figure B-8 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. Stabilization/solidification techniques have been tested successfully on synthetic military waste sludges and simulated pink water. The technology, however, has not been shown to render non-reactive the synthetic sludges containing nitrocompounds such as nitrocellulose. Stabilization/solidification has not been tested on red water or a comparable simulation.
- ° Was the technology evaluated in the 1980 CSL Report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water would be treated after it has left these processes.
- ° Is the process a concentrative rather than a treatment effort? No.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? No. Stabilization/solidification techniques have not been shown to render red water non-reactive, which is a requirement for land disposal. Thus, the treated product would not be suitable for recycle, discharge or disposal, or amenable for further treatment.

Stabilization/solidification is not recommended for further evaluation. Stabilization/solidification may be useful as a final step, following primary treatment by another method.

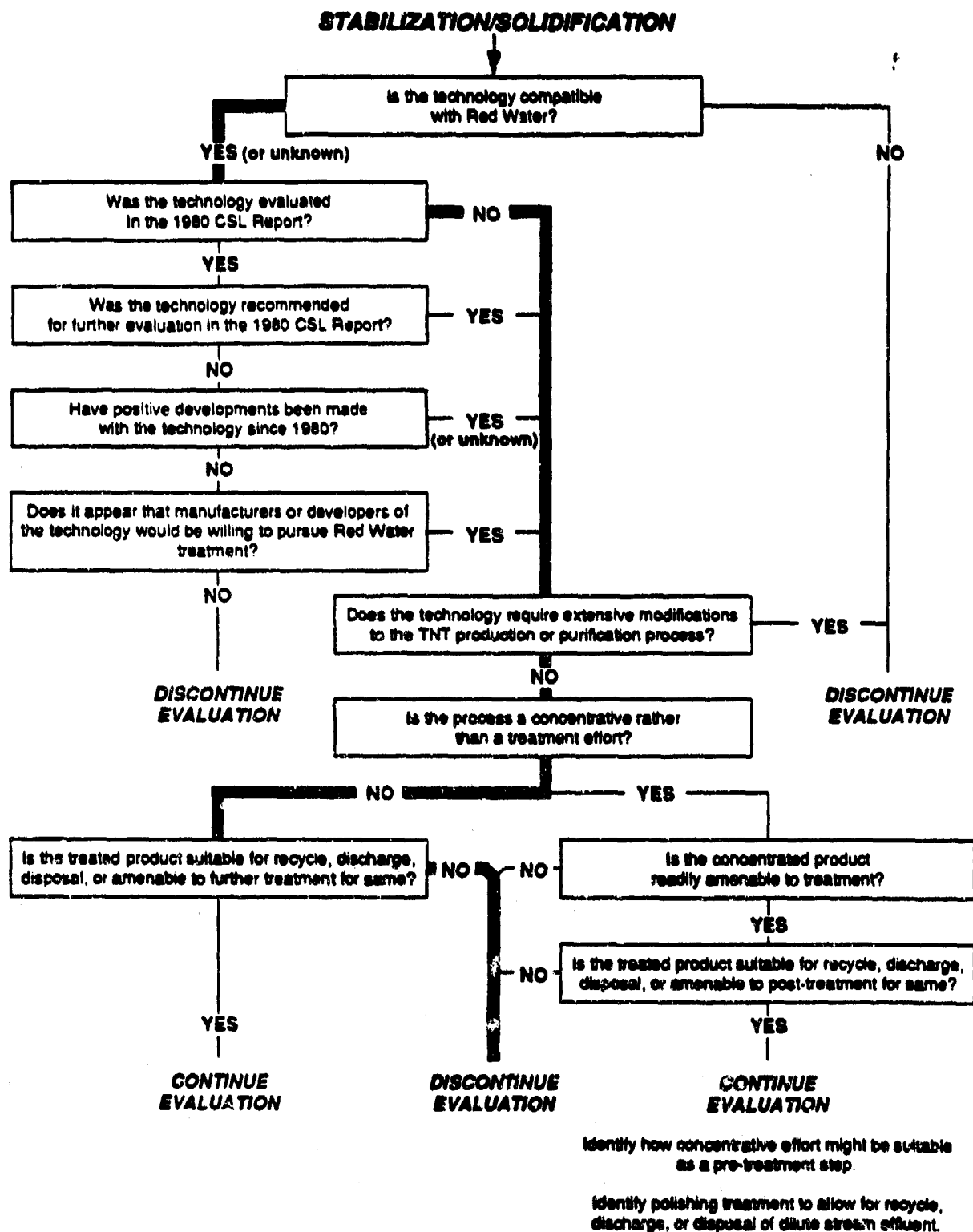


Figure B-8. Prescreening decision tree for stabilization/solidification.

SURFACTANT TECHNOLOGY

Surfactants containing amino or quaternary ammonium groups have been used to precipitate organic compounds similar to those found in red water. Requirements are that the organic molecule must have (1) a benzene ring, (2) a methyl group on the benzene ring, and (3) at least two nitro groups on the benzene ring ortho and/or para to the methyl group. Two organic molecules condense with the linkage being at the methyl group to form a large anion. The cation from the surfactant combines with this anion to form a precipitate.

Scientists at the U.S. Army Armament Research and Development Center (ARDEC, formerly ARRADCOM) in Dover, New Jersey, carried out two-liter laboratory-scale investigations on precipitating TNT, other explosives, and related compounds from dilute solutions (100 milligrams per liter typical) using commercial surfactants (Freeman, 1985). The reactive groups on the surfactant molecules were amino and quaternary ammonium groups. Additional work at Polytechnic Institute of New York was supported by ARRADCOM (Okamoto, et. al., 1982). Investigations were carried out using both synthetic solutions and pink water from the Louisiana Army Ammunition Plant.

Essentially complete precipitation was obtained of organic molecules having a methyl group and at least two nitro groups (ortho and/or para to the methyl group) on the benzene ring. Removal efficiency depended on:

- ° Choice of surfactant
- ° Reaction temperature (the range of investigation was from 25° to 55°C)
- ° pH (range of investigation was from 11 to 12)
- ° Reactor residence time (range of investigation was from 18 minutes to 24 hours)

Preliminary experiments with red water were conducted at the Polytechnic Institute of New York but the work was not continued long enough to determine the applicability of surfactant technology to red water (Carrazza, 1989). The following problems were encountered in the preliminary testing of surfactant technology:

- ° The experiments did not produce a clear effluent. The transition from precipitating from 100 ppm concentrations to up to eight percent organic concentrations may require procedural changes.
- ° The quaternary ammonium surfactant is also toxic and must essentially be completely removed from solution. The surfactant treatments are done in alkaline solution (pH 11 to 12) and the pH must be dropped before discharging the wastewater. Any excess surfactant may be more readily removed in a separate processing step.
- ° Products evolved from incinerating the organic precipitants have not been defined. This includes both air emissions such as nitrogen oxides and also possibly toxic ash. Separating organic and inorganic compounds prior to incinerating the organic compounds will reduce the quantity of ash obtained and will also probably render the ash more amenable to any required subsequent treatment.

A great deal of work requiring considerable time would be required to convert the laboratory scale work with pink water to a process for treating red water. The process parameters that would have to be defined include:

- ° Defining conditions for precipitating all of the organic compounds found in red water. Different surfactants, pHs, temperatures, and reaction times were required to precipitate the compounds found in pink water. Red water has several organic compounds that are not present in pink water, including dinitrotoluene sulfonates. In addition, the concentrations of nitroaromatics in red water is significantly greater than in pink water. Conditions will have to be defined for the precipitation of each of these compounds for the concentrations found in red water. A viable process may require several reactors in series. Precipitating red water organics will probably be more complex than precipitating pink water organics. The investment in process instrumentation and controls may be substantial.
- ° Excessive surfactants will be required to achieve complete precipitation of the red water organics. The excess will also have to be completely removed.
- ° The precipitated organics will have to be separated from the mother liquor with both solids and liquids requiring subsequent treatment. The solids will probably contain significant amounts of entrained mother liquor. This may be more of a problem when the process is scaled up from bench to plant scale.

- ° Satisfactory means of either subsequent treatment or disposal of both precipitated material and also mother liquor will have to be developed, tested, and evaluated.

These obstacles are presently anticipated. Additional obstacles may present themselves as development work progresses. Surfactant technology appears to be complex and would require a very substantial process development program.

The prescreening decision tree for surfactant technology is shown in Figure B-9 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. All work has been done with actual or synthetic waste streams.
- ° Is the process a concentrative rather than a treatment process? Yes. The organic compounds are precipitated and separated from the inorganic compounds. This renders both fractions more treatable.
- ° Are the concentrated products readily amenable to treatment? Yes. The organic precipitates could be incinerated without using supplemental fuel. The organic precipitates might be sufficiently insoluble to landfill or might be biodegradable and treatable by land farming. The inorganic wastes would be more amenable to treatment after having been separated from the organic material. For example, sulfates and sulfites could be precipitated with lime, yielding a solid free of organic matter.
- ° Are the treated products suitable for recycle, discharge, disposal, or amenable to post-treatment for same? Yes. If successful, the effluent would be suitable for discharge. The feasibility of successfully treating the organic precipitates is unknown at this time.

Surfactant technology has survived the decision tree analysis and is recommended for further evaluation. However, its potential appears to be limited.

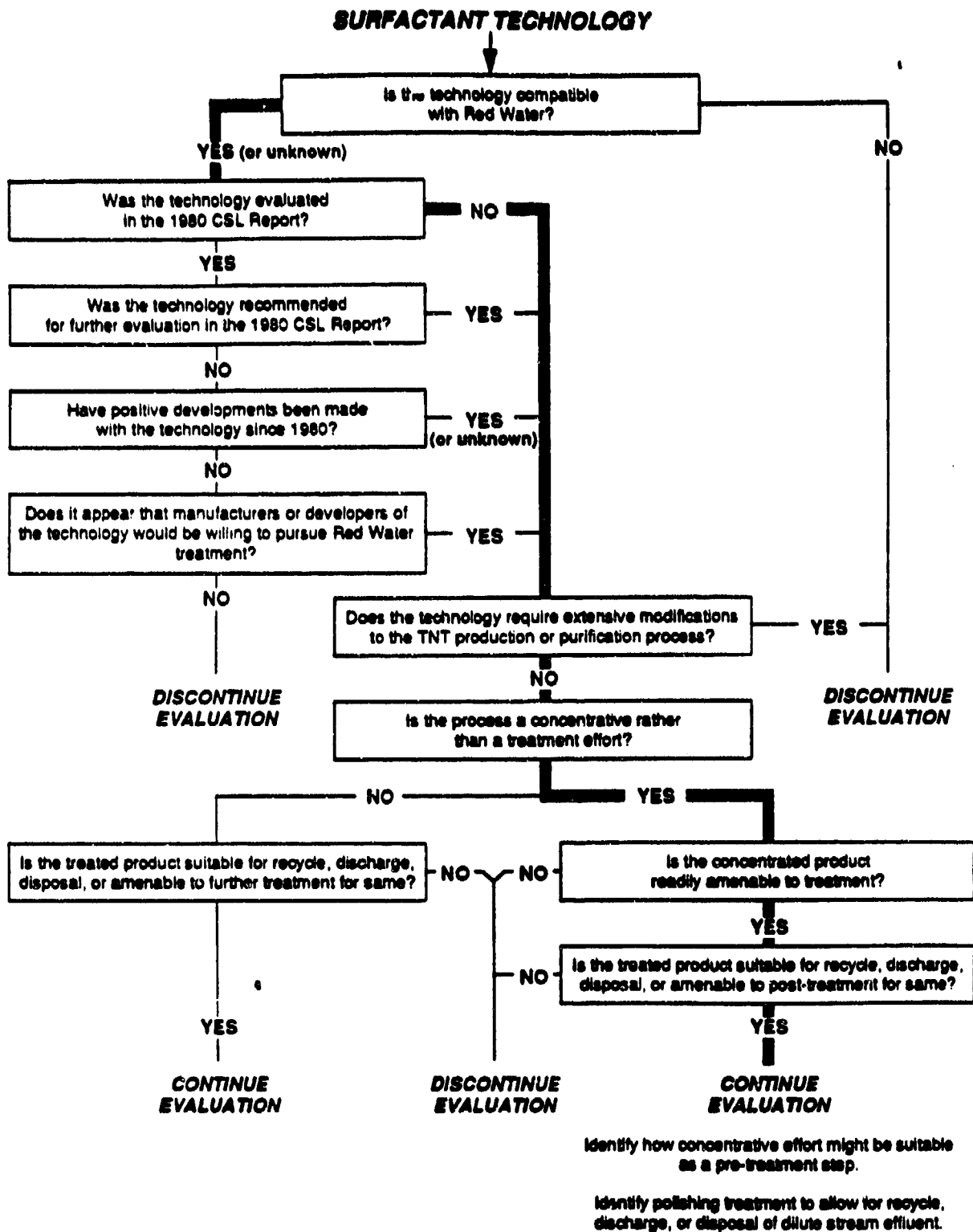


Figure B-9. Prescreening decision tree for surfactant technology.

WET AIR OXIDATION

Wet air oxidation is a process in which organics and/or oxidizable inorganics are mixed in an aqueous solution with air at elevated temperatures and pressures. Lower temperatures (300-390°F) improve sludge dewaterability; intermediate temperatures (390-540°F) are used to regenerate spent activated carbon and to convert refractory compounds to biodegradable substances; and higher temperatures (540-620°F) provide essentially complete oxidation. The higher temperature provides a faster reaction rate and allows the air oxidation of matter that would not normally be oxidizable. An above-atmospheric pressure maintains water as a liquid and also increases the solubility of air (oxygen) in water. Typical reaction pressures are between 300 and 3000 psig. Wet air oxidation has successfully treated a number of wastes, including pesticide wastewater, petrochemical wastes, and propellant wastewaters.

The reactor is a pressure vessel and if used for red water oxidation would probably be constructed of 304 or 316 stainless steel or better. Auxiliary equipment would include a high-pressure pump to bring red water into the reactor, an air compressor to provide high-pressure air, a separator to separate liquids and gases from oxidized red water, and heat exchangers. Sodium sulfite would be converted to sodium sulfate, sodium nitrite would be converted to sodium nitrate, and sodium dinitrotoluene sulfonates would probably be converted to carbon dioxide, water, sodium sulfate, and nitrogen, nitrogen oxides, or sodium nitrate.

The usual oxidation efficiency is better than 95 percent but less than 100 percent. Consequently, subsequent treatment of the aqueous stream from the reactor would be required. This stream would probably be eligible for delisting as a hazardous waste since TNT processing wastes (K047) are so classified because of reactivity rather than the presence of any specific chemical compound.

Zimpro/Passavant, located in Rothschild, Wisconsin, successfully treated samples of pink and red water in the early 1970's (Copa 1989). Mr. Tipton L. Randall of Zimpro/Passavant provided a rough cost estimate of \$2.0 to \$2.5

million for the installed capital cost of a 15-gallon-per-minute unit with all required auxiliaries (this system would be capable of treating 21,600 gallons per day). The treatment effectiveness of wet air oxidation on the red water is still being investigated. Zimpro is currently investigating whether the client on that project claimed confidentiality, and, if not, will send all relevant reports and data.

Wet air oxidation would allow oxidation with air rather than expensive chemicals such as hydrogen peroxide, ozone, or bromide ions and would not have the heavy supplemental fuel cost of a thermal incinerator.

Development work would be required to:

- ° Determine the optimum pressure and temperature. The cost of pressure vessels is very sensitive to the operating pressure. The pressure of superheated water is very temperature-dependent.
- ° Determine required treatment procedures for the process effluent. It would be desirable for the effluent to be treatable in the existing plant wastewater treatment system.
- ° Determine suitable materials of construction for the pressure vessel and auxiliary equipment.

The prescreening decision tree for wet air oxidation is shown in Figure B-10 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Yes. A contact with Zimpro/Passavant has indicated that tests on pink and red water were conducted successfully in the early 1970's.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications by the TNT production or purification process? No. Wet air oxidation would be applied to the red water resulting after the TNT purification process.
- ° Is the process a concentrative rather than a treatment effort? No. If successful, wet air oxidation would treat the red water and render it nonhazardous.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. If successful, wet air oxidation would destroy all hazardous components and provide a treated stream suitable for discharge or conventional biological treatment.

Wet air oxidation is recommended for further evaluation.



C-53

FLUIDIZED BED REDUCTION OF INCINERATION ASH

The evaluation of fluidized bed reduction applies only to the ash resulting from red water incineration. For the purpose of this analysis, we have assumed that red water can be successfully incinerated and the ash can be ground to a uniform particle size. After grinding, the components of the ash are chemically converted to sodium carbonate and hydrogen sulfide.

Sulfate reduction in a fluidized bed produces intermediate products including sodium sulfite (Na_2SO_3), elemental sulfur, and sodium polysulfides (Na_2S_x), which can be considered as elemental sulfur dissolved in sodium sulfide (Na_2S) as well as the desired product Na_2S . In experiments conducted in 1968 and 1969 at Kerr-McGee Corporation, reduction was far short of complete. One explanation was that sodium sulfate and intermediate reduction products formed liquid phases on the particle surface. The liquid surface caused particles to agglomerate, clogging the fluidized bed. Also, reducing gases could not diffuse through the liquid surface, leaving the particle interior unreacted. Bench scale work at Battelle Memorial Institute indicated that agglomeration could be avoided through a two-step scheme but no follow-up work has been published.

Sodium sulfate and other sulfur compounds can be reduced to sulfides by solid and liquid reducing agents such as coal (the LeBlanc Process was patented in 1795) and lignin (pulp and paper industry black liquor). Gas phase reduction does not appear to be feasible.

Sodium salts that could be expected to be found in incinerated red water ash and their melting points are (Handbook of Chemistry and Physics):

Salt	Melting Point	
	$^{\circ}\text{C}$	$^{\circ}\text{F}$
Na_2CO_3	851	1564
Na_2SO_4	884	1623

<u>Salt</u>	<u>Melting Point</u>	
	<u>°C</u>	<u>°F</u>
Na_2SO_3	"decomposes at red heat"	
Na_2OH	318.4	605
Na_2O	sublimes at 1275	sublimes at 2327

NaNO_3 decomposes at 380°C (716°F) and NaNO_2 decomposes at 320°C (608°F) with the expected products being Na_2O and nitrogen oxides. Since incineration takes place at 705°C (1300°F), NaNO_3 and NaNO_2 would be converted to Na_2O . On standing in the presence of moisture (or humid air), Na_2O would form NaOH . Hence, the incineration ash would be alkaline.

Upon incineration, the sodium sulfonates and benzoates found in red water could form mixtures of Na_2SO_4 , Na_2CO_3 , Na_2SO_3 , and NaOH . These would contribute to the overall alkalinity of the ash.

Examples that mixtures of two compounds may have lower melting points than either pure compound include (data are from Gmelins' Handbuch de Anorganischer Chemie):

<u>Compound 1 and MP°C</u>	<u>Compound 2 and MP°C</u>	<u>Melting point of Eutectic</u>
Na_2CO_3 - 851	Na_2S - 1180	795
Na_2CO_3 - 851	Na_2SO_4 - 884	826
Na_2SO_4 - 884	Na_2S - 1180	730

These are simple, two-component systems and the mixtures found in partially reduced red water incineration ash would be much more complex. However, low melting phases that include elemental sulfur (melts at 120°C or 248°F), sodium polysulfides (Na_2S_5 melts at 216°C or 420°F), and other lower melting components are formed. The results are solids that melt during attempted reduction, thus clogging the fluidized bed.

Mr. James Carrazza of the U.S. Army Research and Development Center (ARDEC), Dover, New Jersey, commented that his experience had been that agglomeration and partial reduction were real problems for sulfate reduction in a fluidized bed.

The prescreening decision tree for fluidized bed reduction of incineration ash is shown in Figure C-1 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Yes. We have assumed that incineration, ash collection, and ash grinding are feasible.
- ° Was the technology evaluated in the 1980 CSL report? Yes. Pilot plant investigations were described in the April 1980 report. Results were mixed.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? No. The technology was ranked fourth out of ten. Only the top three candidates were evaluated further.
- ° Have positive developments been made with the technology since 1980? No. We searched Chemical Abstracts from July 1979 to July 1988 and found no further references to published work on the technology.
- ° Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? No. A search of Chemical Abstracts yielded no researchers or manufacturers currently investigating applying fluidized bed reduction to red water incineration ash.

Because fluidized bed reduction was not recommended for further evaluation in the 1980 CSL report and has not undergone any positive developments since that time, this technology is not recommended for further evaluation.

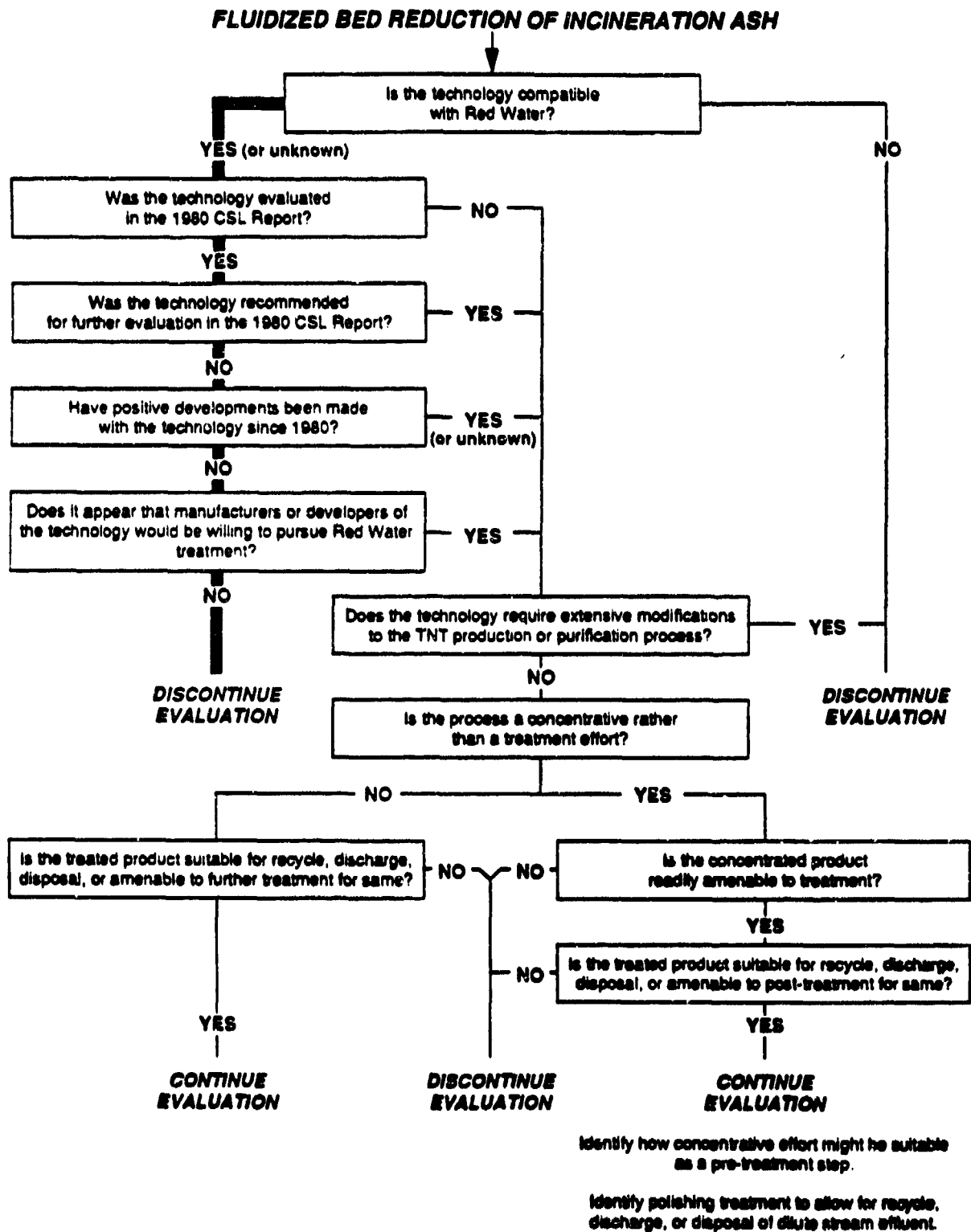


Figure C-1. Prescreening decision tree for fluidized bed reduction of incineration ash.

HYBRID THERMAL TREATMENT SYSTEM (HTTS)

The Hybrid Thermal Treatment System (HTTS), developed by International Technology Corporation (IT), consists of a rotary kiln, a secondary combustion chamber with a water quench chamber, a particulate scrubber system, and other support modules. This combustion system operates below atmospheric pressure in a closely controlled air supply mode; kiln ashes are cooled in a moisture-controlled environment. The kiln gases are incinerated in a vertical secondary combustion chamber, designed to handle large variations in gas composition and volumes and to avoid entrainment of fine solids in the kiln gas. The secondary combustion chamber can operate continuously at 2,200°F. Both the kiln and secondary combustion chamber burners can fire fuel oil, natural gas and/or waste liquids (IT, n.d.).

The secondary combustion chamber gases are quenched with water and then processed through an air pollution control module capable of removing sub-micron particulate matter and acid gases. Treated gases are then pulled through a stack by the induced draft fan. After separation from the scrubber water, solids can be added to the kiln ashes. The scrubber water is then tested and recycled, thus minimizing water consumption. The wastewater effluent can be readily treated prior to discharge.

The HTTS has been used at the Cornhusker Army Ammunition Plant (CAAP) to treat soils contaminated through the leaching of TNT- and RDX-contaminated wastes according to a draft report by Foster Wheeler. The HTTS successfully processed the contaminated soil with discharges meeting required regulations. The vertical secondary combustion chamber was operated at 1,800°F. Downstream of the water quench section, the temperature was 180°F.

IT representatives have proposed a secondary liquid incineration combustion process for red water treatment that would utilize a three-zone thermal combustor to provide staged combustion (Shell, 1989). Zone 1 would

provide an oxidizing environment to destroy aqueous organic wastes; Zone 2 would provide a reducing environment to destroy NO_x , and Zone 3 would provide an oxidizing environment to destroy combustible fumes (H_2 and CO). Combustion gases would be saturated in a water spray contactor, and particulate removal would be accomplished using a variable throat venturi scrubber, followed by a packed bed type mist eliminator. Blowdown would contain Na_2SO_3 , Na_2SO_4 , and Na_2CO_3 . The limiting factor of this secondary combustion process is the volume of gas the air pollution control system can handle, which is 75,000 cubic feet per minute.

Treatment of red water using the HTTS technology has not been investigated, and the effectiveness of this technology on red water treatment is not known. If used for the treatment of red water, this system will require modification to ensure low-level NO_x emissions and to generate an ash that can be delisted or converted to sodium sulfite for reuse in TNT purification.

No information has been obtained regarding the use of the HTTS with liquid wastes. Pretreatment may be required to concentrate red water prior to incineration. Fuel requirements for the combustion of red water using HTTS may be high due to the high water content of the red water.

Waste streams generated during HTTS treatment that may require further treatment include incinerator ash and blowdown water. Metals may pose a significant problem in incinerator ash, as they are concentrated in this and other incineration processes. Blowdown water will require disposal.

The prescreening decision tree for the HTTS is shown in Figure C-2 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. No testing with red water has been conducted; however, testing with soils contaminated with waters resulting from TNT operations has taken place at CAAP.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water waste stream is treated after it has left the TNT production/purification process.
- ° Is the process a concentrative rather than a treatment effort? No. The process, if successful, will destroy aqueous organic wastes, NO_x , and combustible fumes. Particulate matter and acid gases will be removed through an air pollution control system.

HYBRID THERMAL TREATMENT SYSTEM

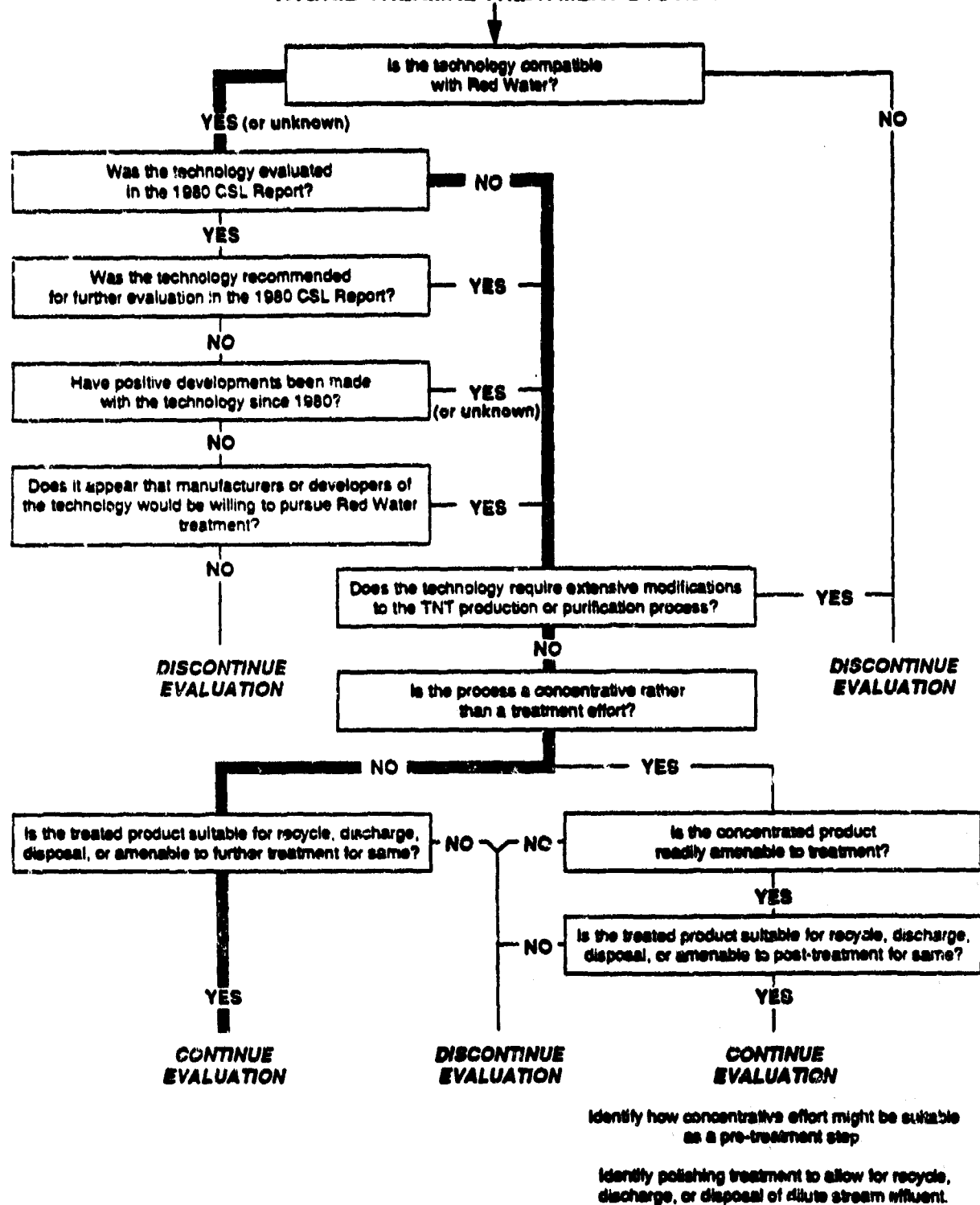


Figure C-2. Prescreening decision tree for hybrid thermal treatment system.

- Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Unknown. Waste streams resulting from the process include incinerator ash and blowdown water.

The HTTS technology has survived the prescreening decision process. Based on the process description and its effectiveness in the destruction of organics, the technology appears to be amenable to treatment of red water at this phase of the evaluation. However, the HTTS incineration process may be eliminated during the secondary screening process if it is determined that the destruction efficiencies of the standard HTTS incineration process are minimal compared to the efficiencies of the secondary liquid incineration system. This may allow the liquid incineration system to be evaluated separately from the HTTS.

INCINERATION BY CANADIAN INDUSTRIES LIMITED (CIL) AT BELOEIL WORKS

Incineration by Canadian Industries Limited (CIL) is a commercially proven technology in operation at the TNT facility at Beloeil, Quebec. The process consists of a multipurpose incinerator that processes a variety of wastes produced at this facility including red water, according to a 1988 draft report by Foster Wheeler. The CIL process includes cyclones to catch dust emissions and a rudimentary scrubber for control of NO_x emissions. Considerable auxiliary fuel is needed to maintain incineration temperatures at approximately $1,000^\circ\text{F}$, according to a CIL representative (Kutuoglu, 1989). The equipment used in the CIL process is similar to the rotary-kiln incinerators that have been previously used at U.S. Army ammunition plants producing TNT.

By-products produced by the CIL incinerator process include ash and gaseous NO_x emissions. The ash resulting from the CIL incineration process is composed of greater than 90 percent sodium sulfate, as well as other constituents such as amorphous carbon and sodium nitrate (Kutuoglu, 1989). Data collected on ash leachate tests from the TNT facility at Beloeil, Quebec, are summarized in Table C-1. Based on TCLP and EP toxicity data, Foster Wheeler representatives contend that ash produced from red water via CIL incineration may be delisted in the United States as nonhazardous (Foster Wheeler, 1988). However, these results do not include testing for reactivity, the characteristic responsible for listing red water as a hazardous waste. Ash resulting from incineration at the CIL facility is landfilled (Dogonaglo, 1989).

There is a great potential during combustion in an oxidizing atmosphere to convert nitrogen-bearing compounds such as those in red water to NO_x . CIL representatives state that NO_x levels in the incinerator stack gas are below the allowable Canadian emission level for NO_x (SO_x is not analyzed). Actual data on air emissions have not been obtained.

TABLE C-1. CONTAMINANT CONCENTRATIONS IN LEACHATE FROM ASH
GENERATED BY RED WATER INCINERATION AT CIL

Constituent	CIL Measurements (mg/L)	EP Toxicity (mg/L)	TCLP (mg/L)
Arsenic	0.009	5.0	5.0
Barium	Not measured	100.0	100.0
Cadmium	0.08	1.0	1.0
Chromium	<0.05	5.0	5.0
Lead	0.62	5.0	5.0
Mercury	0.0007	0.2	0.2
Selenium	0.008	1.0	1.0
Silver	Not measured	5.0	5.0
Phenol	<0.005	---	14.4
TOX	<0.001	---	83.6*
			0.06+

* Summation of TCLP halogenated compounds; however, individual compounds also have limits.

+ Lowest TCLP halogenated compound limit.

Source: Foster Wheeler, 1988.

The CIL rotary-kiln incineration process is used for the combined treatment of a variety of explosive wastes resulting from TNT manufacturing and other explosive operations. The CIL incineration process is nearly identical to incineration that has taken place at U.S. Army ammunition plants producing TNT. One difference between the Canadian and U.S. processes is that an evaporation step has been used at U.S. treatment facilities to concentrate the waste prior to incineration. The CIL process does not include evaporation because the waste is explosive and does not require evaporation as a pretreatment step according to CIL representatives.

In the 1980 CSL report, incineration with ash landfill was evaluated as an option for red water treatment. Incineration at Radford Army Ammunition Plant was eliminated during the CSL evaluation due to several problem areas: condensate disposal, ash leaching, and air pollution. An additional potential drawback of the process is the high cost associated with auxiliary fuels required during incineration.

The prescreening decision tree for incineration by CIL is shown in Figure C-3 and the decision tree analysis is provided below.

- ° Is the technology compatible with red water? Yes. The technology has been commercially demonstrated to incinerate red water.
- ° Was the technology evaluated in the 1980 CSL Report? Yes. Incineration by CIL was not evaluated in the 1980 CSL report. However, the similar U.S. process of incineration of red water and landfilling of the ash was evaluated.
- ° Was the technology recommended for further evaluation in the 1980 report? No. The technology was eliminated due to environmental problems involving condensate disposal, ash leaching, and air pollution, as well as high cost.
- ° Have positive developments been made with the technology since 1980? Yes. The CIL process involves landfill of ash produced by incineration. Positive developments have been made in landfill technology since 1980. However, the waste, a listed K047 hazardous waste, has been banned from landfills in the U.S. Landfill of the ash is viable only if delisting of the ash is accomplished.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water waste stream resulting from production/purification of TNT would be treated.

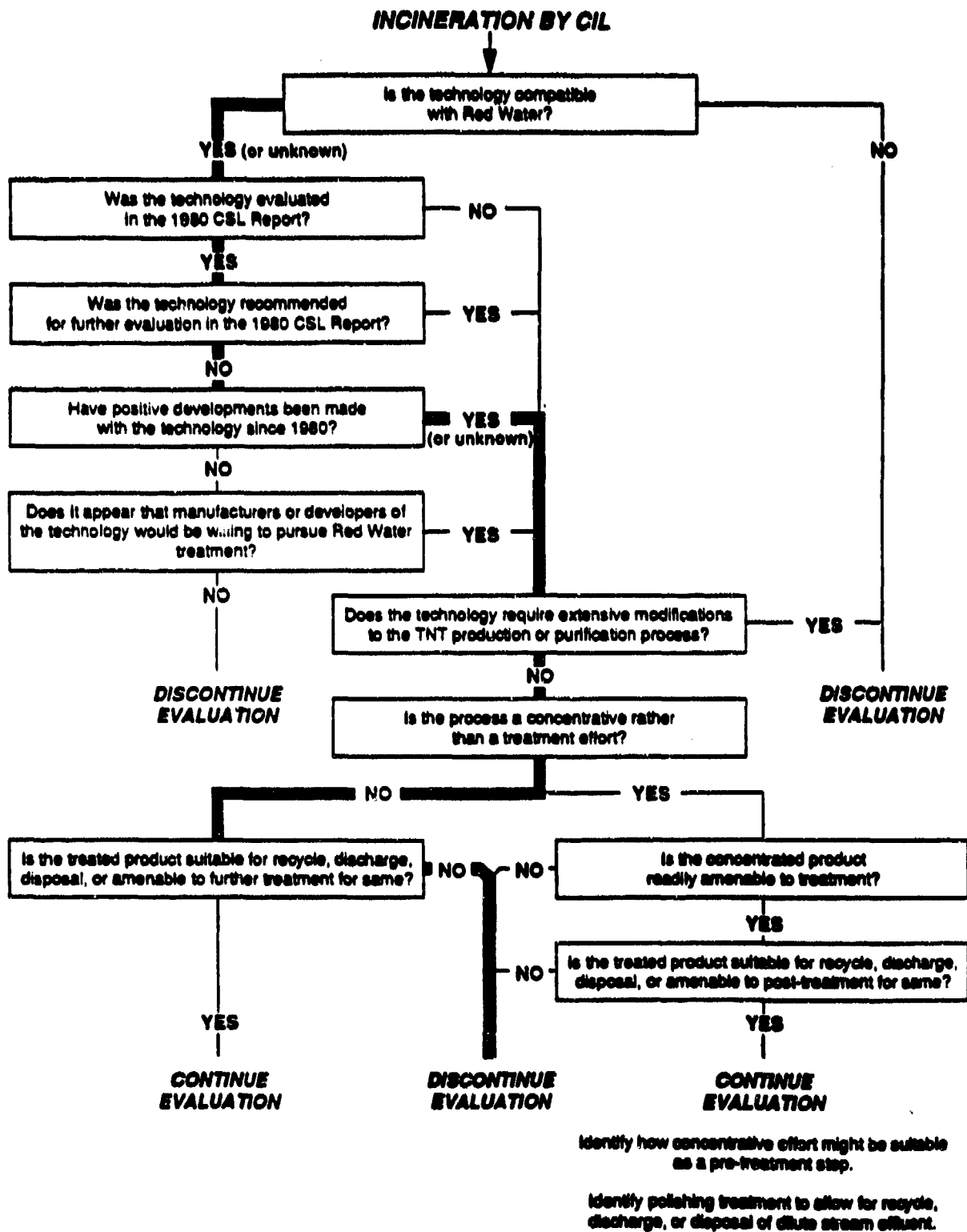


Figure C-3. Prescreening decision tree for incineration by CIL.

- Is the process a concentrative rather than a treatment effort? No. The process destroys organic wastes by incineration.
- Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? No. Due to leachability of the ash resulting from the CIL process, landfilling the ash without additional treatment is not a viable method of disposal.

Based on evaluation of the CIL process, it appears that incineration and landfilling of resulting ash will not be a viable process for red water treatment. Because ash treatment technologies are being evaluated elsewhere in this analysis, incineration by CIL will not be evaluated further during the secondary-level evaluation of red water treatment technologies. Hence, incineration by CIL has not survived the prescreening decision process.

PLASMA ARC

Plasma arc is a thermal destructive process whereby organic materials are converted to inorganic by-products. The heat source is an electric arc that maintains a temperature of several thousand degrees centigrade, which can convert a material to plasma. Plasma is often called the fourth state of matter and is characterized by molecules even further separated than in gases. Inorganic by-products of this process are formed upon recombination of atomic species. The process is typically performed in the absence of oxygen, thus minimizing NO_x and SO_x production in nitrogen- and sulfur-rich materials.

Three manufacturers of plasma arc processes are identified in a draft report by Foster Wheeler on red water disposal: Westinghouse Plasma Systems Inc. (Westinghouse-PSI), Tetronics Research and Development Company, and SKF Plasma Technologies. The Westinghouse-PSI and Tetronics systems operate under the same general principle whereby materials are exposed directly to the electric arc. The SKF process differs in that a carrier gas is passed through the torch where it picks up energy from the arc and then transfers the high energy gas to the reaction zone in a furnace.

The Tetronics process was designed for application in the materials and metallurgical industries, and the SKF process was designed for the recovery of black liquor in the pulp and paper industry. Both of these processes are utilized in industry for these respective applications. It is not known whether destruction of organic wastes using these processes has been evaluated. However, based on the available process descriptions, these processes do have potential for organic waste destruction. SKF has a pilot unit available for performing tests with red water at its testing facility. Although Tetronics has a testing facility, a plasma test unit would have to be constructed to evaluate red water treatment with the Tetronics process.

The Westinghouse-PSI process is the only one of the three methods for which reference to destruction of organic wastes has been made. Two trial burns were discussed in a 1986 Alliance Technologies Corp. report to the U.S. Environmental Protection Agency (EPA). During a test burn with carbon tetrachloride, greater than 99.99 percent destruction occurred. A trial burn with PCBs resulted in a destruction efficiency of greater than 99.9999 percent. Westinghouse-PSI has a prototype unit that can be used for pilot tests.

It is unknown if treatment of red water using the Westinghouse-PSI process has been tested. Westinghouse-PSI, did, however, perform mass and energy balances for its prototype unit to determine red water by-products. Based on the mass balance, a scrubbing system prior to release of the gas phase will be necessary for removal of the sulfur-containing compounds. Components retained in the aqueous phase formed upon atomic recombination are amenable to conventional treatment processes.

The prescreening decision tree for plasma arc technology is shown in Figure C-4 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. Plasma arc technology has not been tested on red water.
- ° Was the technology evaluated in the 1980 CSL Report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No.
- ° Is the process a concentrative rather than a treatment effort? No. Plasma arc processes involve thermal destruction of organic compounds in waste streams. Therefore, the process is a treatment effort.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. Off-gases can be effectively treated using scrubbing control systems; conventional wastewater treatment processes can be used for management of aqueous wastes.

The plasma arc technology has survived the go/no-go decision tree analysis. Based on process descriptions, theoretical modeling, and its effectiveness in the destruction of organics, the technology appears to be amenable to treatment of red water at this phase of the evaluation.

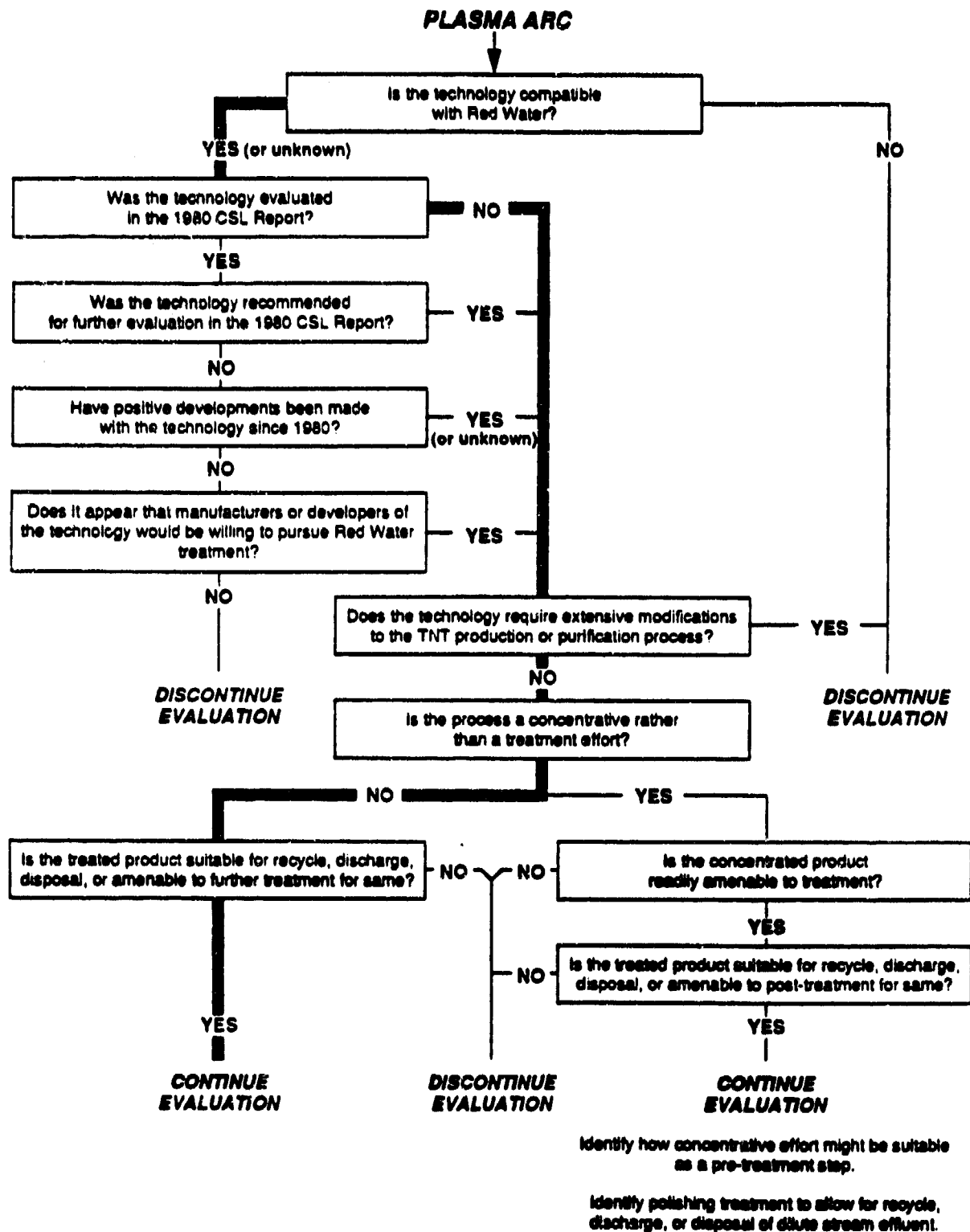


Figure C-4. Prescreening decision tree for plasma arc.

SCA BILLERUD RECOVERY

The SCA Billerud Recovery process was evaluated in the 1980 CSL report. The technology was developed by SCA Development in Sundsvall, Sweden. The process was developed for the pulp and paper manufacturing industry and was used in at least six plants around the world by 1980. In this process, spent "black liquor" is concentrated to 52 to 55 percent solids and sprayed into a pyrolyzing reactor operated at 1,300 to 1,400°F. The outlet stream consists of combustible sulfur gases (mostly hydrogen sulfide), inorganic dust (sodium carbonate), and carbon particulates. The gas stream is passed through a waste heat boiler for steam generation and then through a cyclone to recover dust. The cleaned gas, with a heating value of 100 Btu per cubic foot, is burned in a boiler where sulfur dioxide is generated. The recovered dust, consisting of sodium carbonate and carbon, is slurried and vacuum filtered to remove carbon particulates from the sodium carbonate solution. Finally, sodium sulfite (sellite) solution is generated for the paper pulping process by scrubbing the sulfur dioxide from the gas stream with the sodium carbonate solution in an adsorption tower.

In the 1980 CSL report, this process was ranked eighth out of the ten technologies evaluated. Two potential contacts, the Lummus Crest Company (a subsidiary of Combustion Engineering and the architectural and engineering firm for the installation of the Mead Corporation SCA Billerud recovery plant) and Combustion Engineering (a firm which until recently had a licensing agreement with the Swedish development company to sell the process in the United States), were identified in the 1980 CSL Report. Both of these firms were contacted to determine if advances in the process have been made since 1980. Representatives of both firms were not familiar with the process and could neither answer technical questions nor suggest a technical contact (Lummus Crest Company, 1989; Combustion Engineering, 1989).

Mr. James Carrazza of the U.S. Army Armament Research and Development Center (ARDEC) was contacted to inquire if he knew of any technical contacts

for the process (Carrazza, 1989). He did not know of any firms actively marketing the process in the United States and was not able to suggest a manufacturing or marketing contact. He also stated that there were numerous problems with the process and it was probably not a good candidate for treatment of red water, and should therefore not be evaluated further. Mr. Carrazza suggested that the SCA Billerud recovery process was not evaluated in the February 1988 Foster Wheeler draft report because a technical contact could not be located at that time. He was sure that no testing of the SCA Billerud process with red water had been performed since 1980.

The decision tree for the SCA Billerud recovery process is shown in Figure C-5, and the decision tree analysis is provided below.

- ° Is the technology compatible with red water? Unknown.
- ° Was the technology evaluated in the 1980 CSL Report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL Report? No. The SCA Billerud recovery process ranked eighth out of the ten technologies evaluated and was not recommended for further evaluation.
- ° Have positive developments been made with the technology since 1980? No. Because it was not possible to contact a technical expert for this process, it is unlikely that positive developments have been made with the process since 1980.
- ° Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? No. Because it was not possible to contact a technical expert for this process, it is likely that manufacturers or developers of this process are not interested in pursuing red water treatment.

This process has not survived the go/no-go evaluation and will not be investigated further. Considering the low ranking of the process in the 1980 CSL Report, the fact that a technical contact for the process could not be located, and the discussion with Mr. Carrazza, the process does not seem applicable for treatment of red water.

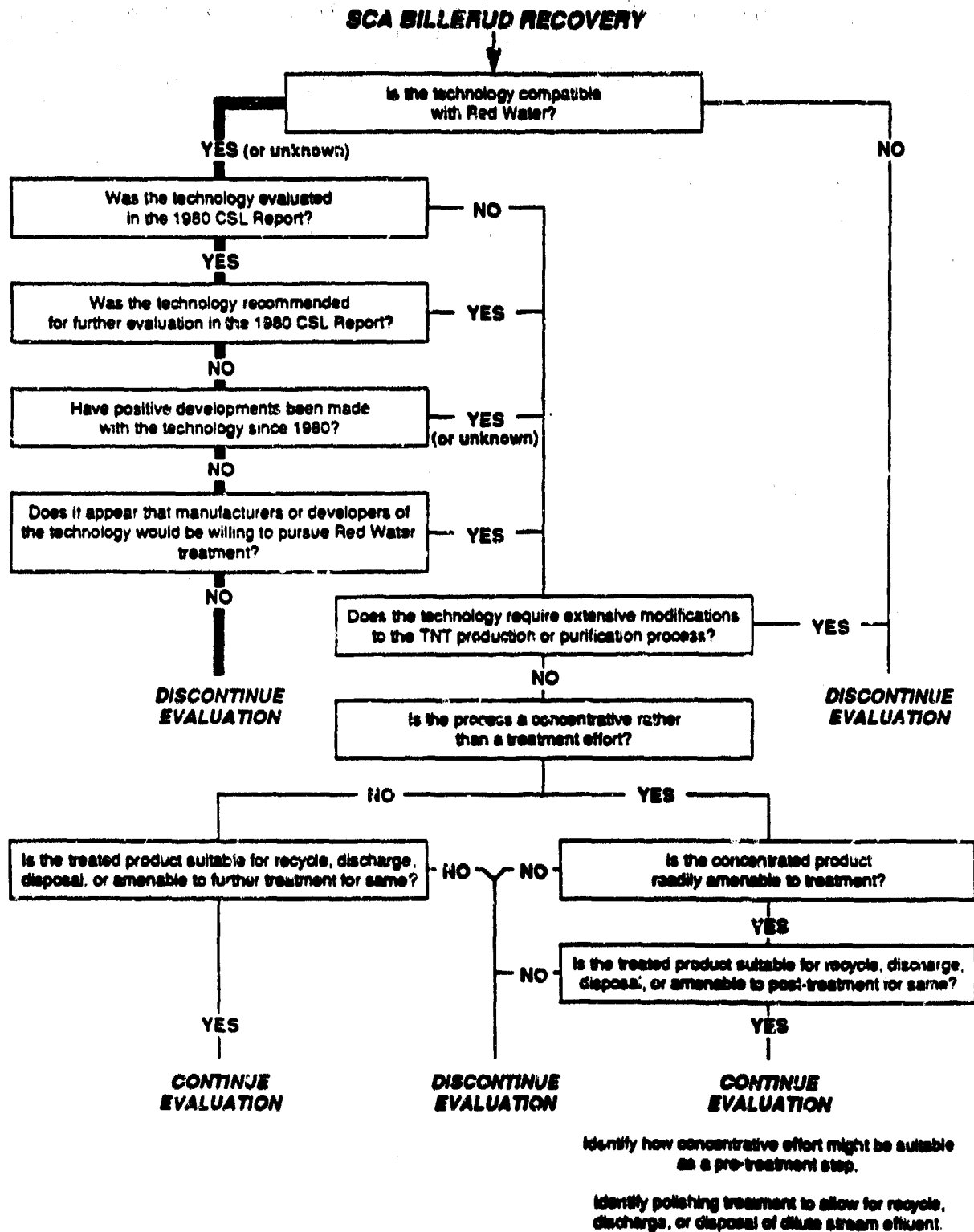


Figure C-5. Prescreening decision tree for SCA Billerud recovery.

SLAGGING ROTARY KILN

Incineration by slagging rotary kiln (SRK) is a process that operates at a higher temperature than standard rotary kilns. Temperatures in the primary incineration chamber of any SRK generally range from 2,000° to 2,400°F (Devin, 1989). The higher temperature enables more complete combustion of the waste and encapsulation of constituents in the generated ash. Therefore, the SRK ash and slag are much more resistant to leaching when compared to ash produced from standard incineration processes. The process produces inert wastes in the molten form.

The SRK system may be equipped with a liquid incinerator for additional processing of exhaust gases from the rotary incinerator along with thermal destruction of liquid waste. An afterburner provides additional residence time in an excess air environment to destroy organic compounds in the gas stream. NO_x present in the gas stream leaving the afterburner will be removed with a denox reactor. An evaporative cooler reduces the temperature of the hot gas stream to 400°F. The quench tank saturates the gas stream with recirculated water, neutralizes some of the acids, and agglomerates and removes coarse particulates. A neutralization system can be provided for applications requiring neutralization of an acidic exhaust airstream. A scrubber system removes inert, organic, and inorganic particulates from the gas stream (Combustion Engineering, 1989).

The SRK technology has not been tested using red water. Commercial slagging rotary kilns have been used in Switzerland for burning a variety of mixed wastes; however, the content of wastes burned is not known at this time.

Disadvantages of the SRK, compared with standard incineration processes, include a higher capital investment, greater operation and maintenance costs, and a shorter refractory life. Additionally, prior to treatment using

SRK red water may require extensive pretreatment to increase the solids content.

The decision tree for SRK technology is shown in Figure C-6 and the decision tree analysis is provided below.

- ° Is the technology compatible with red water? Unknown. To date, testing of SRK with red water has not been conducted.
- ° Was the technology evaluated in the 1980 CSL report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water waste stream is treated after it has left the TNT production/purification process.
- ° Is the process a concentrative rather than a treatment effort? No. The process, if successful, will destroy aqueous organic wastes, NO_x , and combustible fumes and will neutralize and remove particulates in the air stream.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. Organic compounds and NO_x in the gas stream are removed through the afterburner, denox reactor, and scrubber. The process will produce ash with a high resistance to leaching.

The SRK technology has survived the prescreening decision process. Based on the process description and demonstrated effectiveness in waste destruction at this phase of the evaluations, the technology appears to be amenable to treatment of red water.

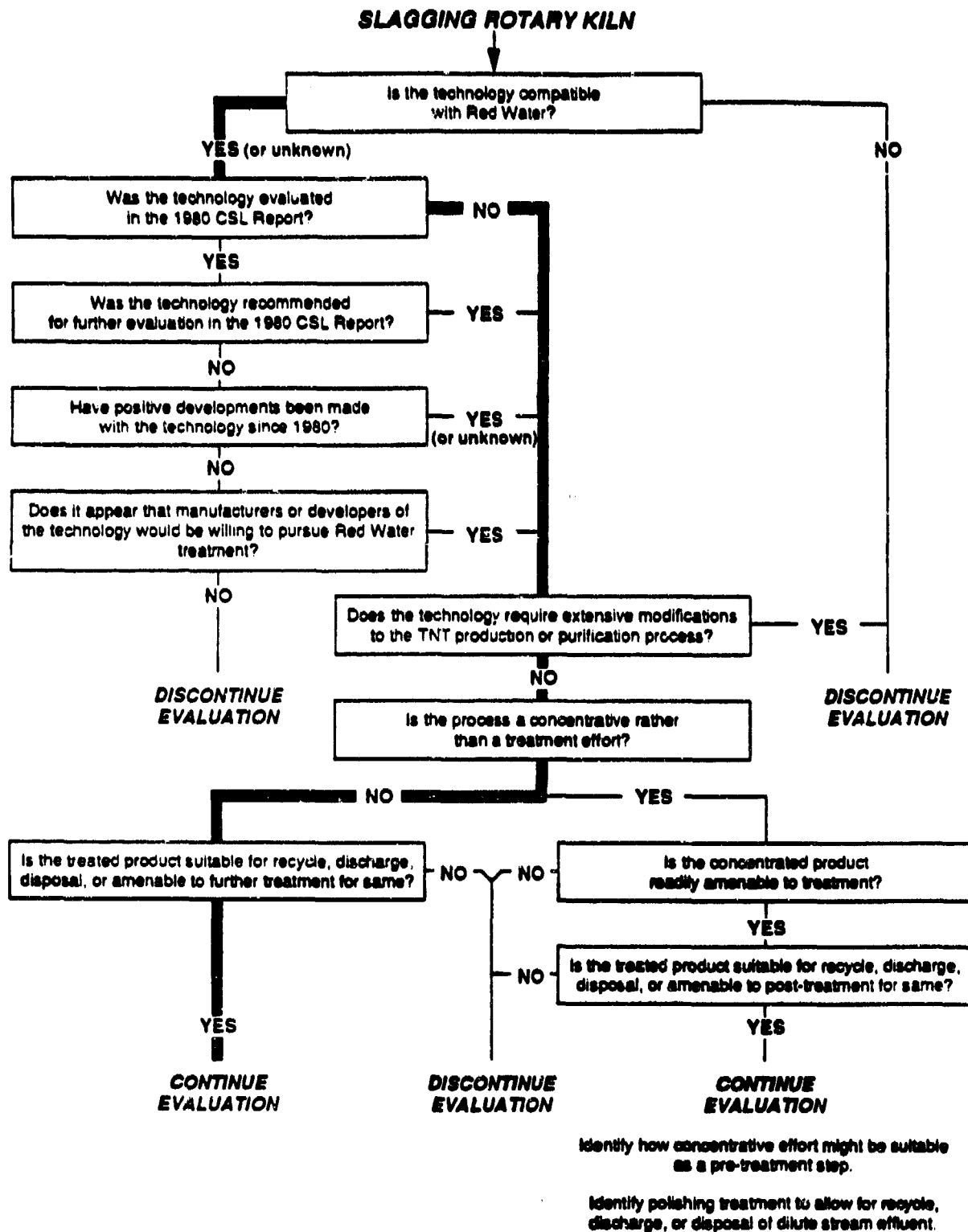


Figure C-6. Prescreening decision tree for slagging rotary kiln.

SUBMERGED COMBUSTION PROCESS

Submerged combustion is a thermal treatment technology that employs a liquid injection slagging furnace for destruction of organic wastes. The difference between this process and conventional liquid injection incineration processes is the temperature at which waste is burned. In submerged combustion, liquid waste is introduced to the furnace where it is burned at a temperature high enough to melt salts that are formed in the process. An auxiliary fuel is used to sustain combustion. The amount of fuel required is mainly a function of the liquid flow rate (i.e., waste flow) into the treatment unit. Because the processing temperature exceeds the melting point of the newly formed salts, the molten salts can be removed easily from the furnace. The process minimizes salt build-up and fouling. The molten salt is drained into a water bath, thus yielding a highly saline solution that can be discharged to a wastewater treatment facility or can be dried to yield a salable salt cake. As is the case for most incineration processes, the effluent gases may require particulate removal, acid gas neutralization, and NO_x reduction.

Representatives of Enviresponse have indicated that the submerged combustion process is capable of 99.99 percent reduction of many organic compounds. Treatment of red water using the submerged combustion process has not been investigated. Therefore, the treatment of red water in the submerged combustion process is strictly conceptual at this time. A submerged combustion test facility is available for the evaluation of red water treatment. Enviresponse representatives have indicated that red water testing at the manufacturer's test facility could generate the necessary data for delisting by-products from the process, thus rendering process residues categorized as nonhazardous wastes.

The prescreening decision tree for submerged combustion is shown in Figure C-7 and the decision tree analysis is provided below:

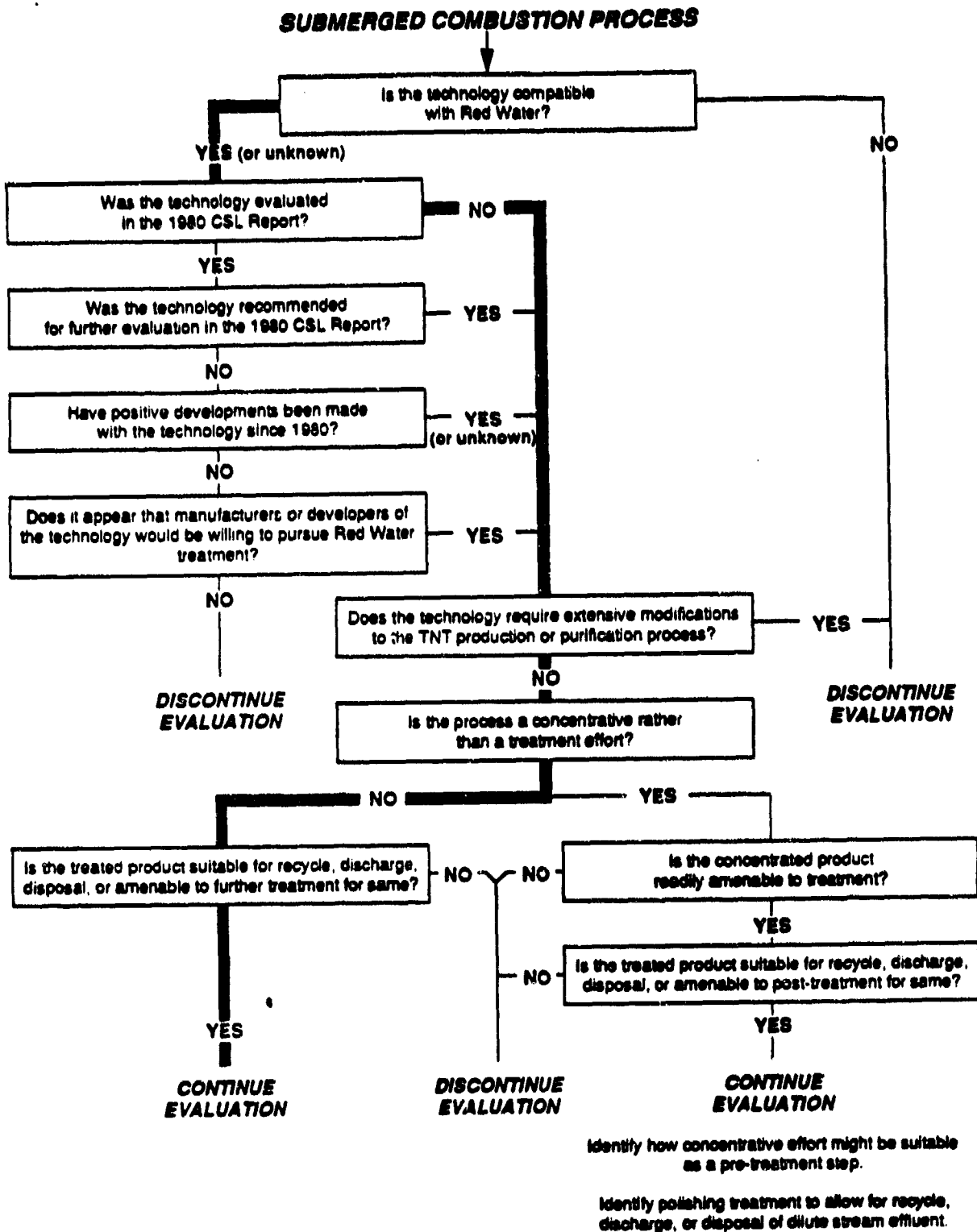


Figure C-7. Prescreening decision tree for submerged combustion process.

- ° Is the technology compatible with red water? Unknown. Submerged combustion has not been tested on red water.
- ° Was the technology evaluated in the 1980 CSL Report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. Red water produced in the TNT purification process would be treated by the submerged combustion process.
- ° Is the process a concentrative rather than a treatment effort? No. The submerged combustion process is a thermal destructive treatment process that allows combustion of organic materials, thus forming inorganic byproducts. Therefore, the process is a treatment effort for destruction of organic compounds.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. The effluent gases may require particulate removal, acid gas neutralization, and NO_x reduction. It is likely these efforts can be accomplished using gas scrubbing systems utilized at conventional hazardous waste incinerators. Assuming the waste products can be delisted, the saline water can be discharged to a wastewater treatment facility or dried to form a salable salt cake.

The submerged combustion process has survived the go/no-go decision tree analysis. Based on the process description and discussions with Enviresponse representatives, the technology appears to be amenable to treatment of red water at this time.

SUPERCRITICAL WATER OXIDATION

Supercritical water oxidation (SCWO) is a process whereby organic compounds are oxidized to inorganic compounds. The fundamental difference between SCWO and conventional oxidation processes is the physical state at which the material is maintained prior to the initiation of the oxidation reaction. In the SCWO process, a liquid is subjected to extreme temperatures (above 374°C) and pressures (215 bar or 212 atmospheres) that elevate the liquid to a supercritical state. Oxygen is an extremely effective oxidant at this state where there is no distinction between gases and liquids. Therefore, when compared to conventional oxidation processes, the greater efficiency of this process is due to the introduction of oxygen at conditions that optimize oxidation kinetics.

The application of this process for oxidation of waste organic materials requires moderate to high pressure reactor vessels, efficient heat exchange, the ability to dissolve stoichiometric oxygen into the reaction vessel, and sufficient Btu value of the organic waste stream to support the heat losses of the process. When toxic or hazardous organic chemicals are subjected to the SCWO process, carbon is converted to carbon dioxide and hydrogen is converted to water. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitrogen compounds will produce nitrogen gas, sulfur is converted to sulfates, and phosphorous to phosphates.

Two vendors of SCWO processes are MODAR and Oxidyne. The MODAR system operates as a closed system that is self scrubbing. The process utilizes pure oxygen and may require an auxiliary fuel if wastes to be destroyed do not contain sufficient heating value to support heat losses to the process. With this process, emission controls are not needed because the inorganic contaminants remain in the liquid phase. Theoretical and bench-scale tests performed by MODAR defined destruction efficiencies for eight groups of compounds. A 99.993 percent removal rate was achieved for 2,4-dinitrotoluene

at 1065°F. It is unknown if any full-scale testing has been performed since the release of the draft Foster-Wheeler report, which referred to MODAR and Oxidyne.

Treatment of red water using the MODAR SCWO process has not been investigated, and therefore remains strictly conceptual. Based on a materials balance and thermodynamic modeling of red water treatment in the process, carbon dioxide and nitrogen would be the only compounds expected to be released in the off-gases. Sodium sulfate is the only compound expected to be present in the wastewater generated by this process.

The principal differences between the Oxidyne process and the MODAR system are in the reaction configurations. The Oxidyne process provides an alternative to aboveground processes by the use of 10,000 to 12,000 feet of natural hydrostatic head feasible in deep well reactors. As in the MODAR process, the Oxidyne process utilizes pure oxygen and may require an auxiliary fuel if wastes to be destroyed do not contain sufficient heating value to support heat losses to the process. Literature on the Oxidyne process presented in the draft Foster Wheeler report indicates destruction efficiencies ranging from 99.99 to 99.9999 percent. However, the only test data available for this system were tests performed with sewage sludge in a 1,500-ft reactor, which yielded greater than 80 percent chemical oxygen demand removal. It is not known if testing has been performed on wastes containing hazardous organics.

The prescreening decision tree for supercritical water oxidation is shown in Figure C-8 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. Considerable concern exists about the safety of placing a concentrated, explosive stream into a system involving highly elevated pressures and temperatures.
- ° Was the technology evaluated in the 1980 CSL Report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The SCWO technology would be applied to the red water effluent from the TNT purification process.
- ° Is the process a concentrative rather than a treatment effort? No. SCWO is a process whereby organic contaminants are oxidized to inorganic compounds. The process is a treatment effort for destruction of organic compounds.

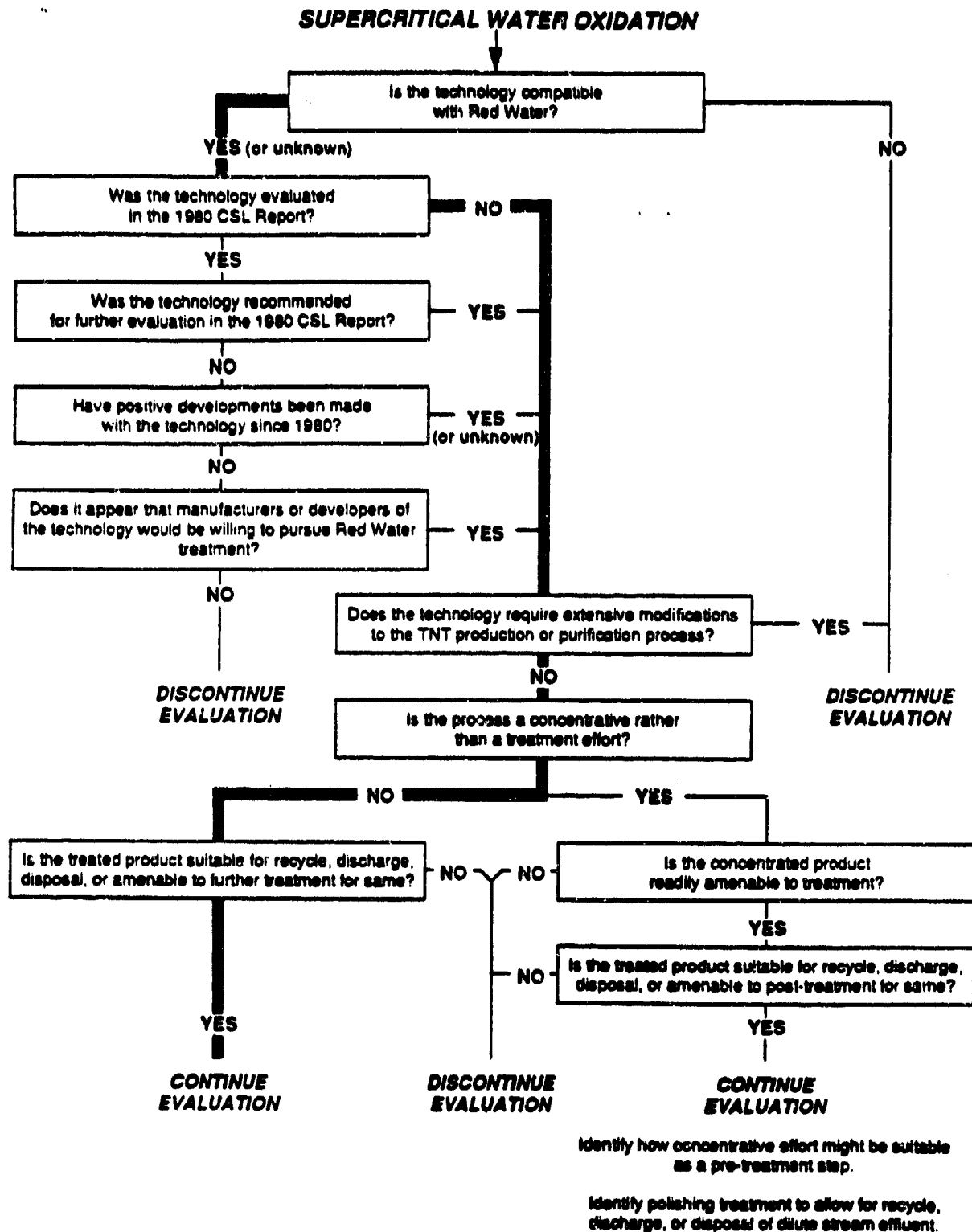


Figure C-8. Prescreening decision tree for supercritical water oxidation.

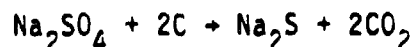
- Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. Nitrogen and carbon dioxide are anticipated to be the only gases liberated from the treatment process. It is not expected that emission controls will be necessary for these gases. The liquid phase by-product of treatment will consist of water and sodium sulfate; the sodium sulfate in the water is amenable to removal by several conventional processes.

The SCWO technology has survived the go/no-go decision tree analysis. Based on the process description, theoretical modeling, and its effectiveness in the destruction of organics, the technology appears to be amenable to treatment of red water at this phase of the evaluation.

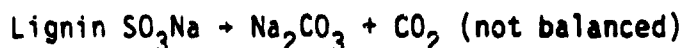
TAMPELLA RECOVERY PROCESS

The Tampella Recovery Process was evaluated in the 1980 CSL report. The technology converts the sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3) from a conventional Kraft recovery furnace to sodium sulfite (Na_2SO_3). As applied to red water, this process is a sodium sulfite regeneration process, not a treatment system. The first step of the Tampella process is a furnace that destroys all the organic compounds. Steps in the Tampella Recovery Process are:

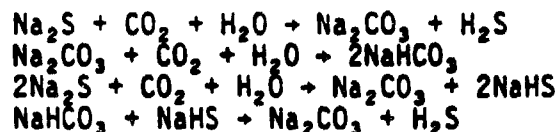
- ° In the Kraft furnace, carbon from decomposing organic matter reduces both inorganic and organic sulfur compounds:



Sodium lignin sulfites (wood pulp is the lignin source) are converted to sodium carbonate:



- ° Na_2S and Na_2CO_3 are treated with carbon dioxide (CO_2) to produce hydrogen sulfide (H_2S) and sodium bicarbonate (NaHCO_3). Sodium bicarbonate may precipitate.



- ° H_2S is stripped from "green liquor" and burned to sulfur dioxide (SO_2).



- ° SO_2 is absorbed in a Na_2CO_3 solution to form Na_2SO_3 solution, which is recycled.



Red water contains sodium sulfate, sodium sulfite, sodium nitrate, sodium nitrite, and sodium dinitrotoluene sulfonates. There is insufficient

organic matter to carry out the reductions and conversions. Carbon would have to be added, probably as coal.

In the sulfate and sulfite reductions within the Kraft furnace, intermediate reduced sulfur compounds, including thiosulfates ($\text{Na}_2\text{S}_2\text{O}_3$), polysulfides (Na_2S_x), and elemental sulfur will be formed. Consequently, there would be prospects for the system to contain carbon, sulfur, reduced sulfur compounds, inorganic nitrates and nitrites, and organic nitro compounds. This mixture of components has similarities to gunpowder, a mixture of carbon, sulfur, and nitrates. Explosions are a possibility.

Tampella technology does not treat organic nitro compounds but recovers and recycles sodium sulfite. The technology carries the implicit assumption that all organic nitro compounds are destroyed in the Kraft furnace.

A Kraft furnace can not necessarily operate on red water and carbon feed in exactly the same manner as on black liquor. A development program would be required to evaluate and determine Kraft furnace feed rates, operating parameters, emission controls, suitable carbon type and nature, and disposition of waste streams. The fate of nitrogen in the organic and inorganic nitrogen compounds would also need to be determined.

Tampella technology is complex and patented. The Army would probably need to purchase technical support and engineering services from Tampella in Europe. Even though a Radford plant would be 1/75th the size of a full scale plant, the level of technical services and support required would be equivalent to that of a full scale facility and proportionally expensive.

The Tampella Recovery Process was ranked sixth out the ten technologies evaluated in the 1980 CSL report. It was determined that red water could be processed in a Kraft furnace based on the successful treatment of red water in a Kraft furnace when the Radford Army Ammunition Plant was operating. However, then the red water was extensively diluted with paper plant "black liquor". In a Tampella process at a TNT plant, the feed to the analogue of a Kraft furnace would be exclusively red water. Process conditions may be very different and could require an extensive development program.

Recent telephone interviews with Ford, Bacon, and Davis, who hold American licensing rights to Tampella technology, indicate that no significant technological advances have taken place since 1980 and there are still no

American plants using the technology (Ford, Bacon, and Davis, 1989). Consequently, the situation is unchanged since the 1980 CSL evaluation.

The decision tree for the Tampella Recovery Process is shown in Figure C-9, and the decision tree analysis is provided below.

- Is the technology compatible with red water? Unknown. Tampella technology has not been applied to red water.
- Was the technology evaluated in the 1980 CSL report? Yes.
- Was the technology recommended for further evaluation in the 1980 CSL report? No. The Tampella recovery process was ranked sixth out of the ten technologies evaluated. Only the top three technologies were recommended for further evaluation.
- Have positive developments been made with the technology since 1980? No. A recent telephone interview with representatives of Ford, Bacon, and Davis (FB&D), who hold American licensing rights to Tampella technology, disclosed that the technology has not changed and no plants in the United States are using the technology. FB&D was interested in Tampella technology because Tampella paper machines were being installed in the United States.
- Would the manufacturers of the technology be willing to pursue red water treatment? No. FB&D did not indicate any interest in pursuing red water treatment.

Because the 1980 CSL report recommended that the Tampella recovery process not be evaluated further, and because no positive developments have been made since, this technology is not recommended for further evaluation.

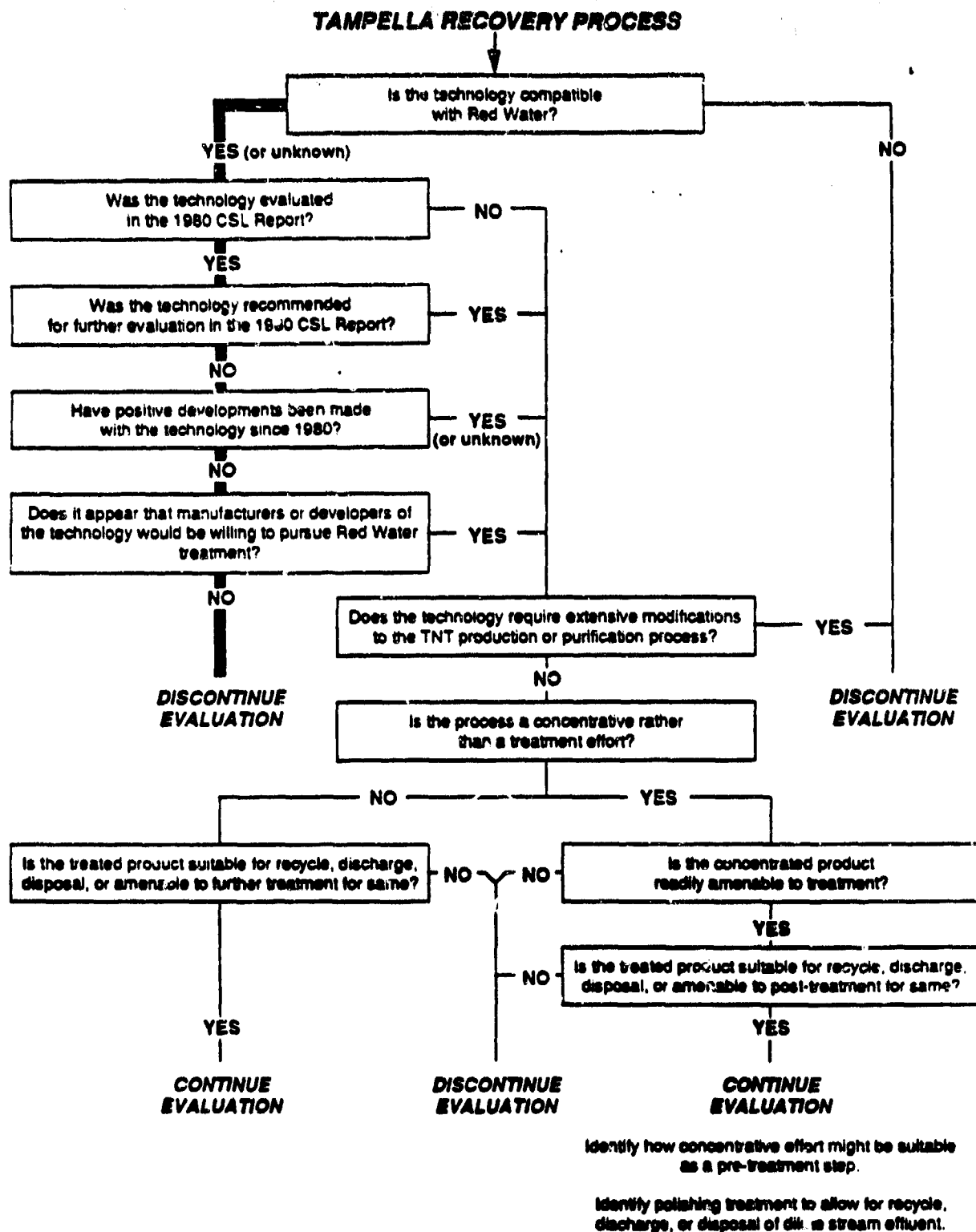


Figure C-9. Prescreening decision tree for Tampella recovery process.

THERMAL SEPARATION

Thermal separation, an International Technology Corporation (IT) technology, is a process whereby an indirectly heated thermal separator unit treats wastes containing hazardous organic contaminants at temperatures sufficient to vaporize the organic components. A similar technology, low temperature thermal treatment, has been developed by Weston Services, Inc. Temperatures in these devices are lower than those used in standard incinerators. Because heating is indirect, a small volume of gaseous materials leaves the separator unit. The organic vapors in the separator off-gas can be treated either by fume incineration or by condensation/scrubbing.

Thermal separation has been demonstrated on pilot and full-scale systems for treatment of soils and solids contaminated with organic compounds including PCBs, PCDDs, PAHs, chlorinated solvents, petroleum hydrocarbons, and pesticides (Fox, 1988). The Weston low temperature thermal treatment system has been demonstrated on pilot- and full-scale systems for treatment of soils and solids contaminated with chlorinated solvents and petroleum hydrocarbons. However, the technologies have not been tested on liquid wastes in general, or red water specifically. For the treatment of red water using thermal separation, IT representatives have proposed using a rotary calciner as the thermal separation device. The rotary calciner is an indirectly heated metal alloy, capable of processing solids at temperatures up to 600°C. The calciner has been used to thermally decompose the nitrate salts of radioactive materials in aqueous solutions with recovery of the nitrogen oxide gases as nitric acid, leaving radioactive oxide solids for waste disposal. If nitrobody-free sodium sulfate cannot be reduced cost-effectively in the calciner, a second stage of waste treatment consisting of incineration in a small rotary kiln could be used to achieve the desired performance. Gases leaving the calciner will contain NO_x compounds, steam, and decomposed organics. Gases could be treated in a system that first condenses the steam and most of

the organics, with the NO_x being collected in a scrubbing system for recovery of nitric acid. Any noncondensable organics could be treated in a fume incinerator. The condensed water and organics should be treatable by conventional means, such as biological oxidation.

Advantages of thermal separation, compared to rotary-kiln incineration, are as follows:

- ° A low volume of gas is produced in the calciner, enabling recovery of nitrogen oxides as nitric acid by using scrubbing technology.
- ° Organics are decomposed and end up either in the water condensate for conventional treatment or in the low volume noncondensable gases for treatment by fume incineration.
- ° The calciner surface, constructed to specially fabricated metal alloy, can withstand direct injection of the red water onto the hot surfaces.
- ° Operating temperatures can be adjusted to below softening/fusion points of the salts produced.

By-products produced from the technology include acidic condensate water resulting from the gas treatment system and the solid residue resulting from the thermal separator unit.

The decision tree for thermal separation is shown in Figure C-10 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. The technology has not been tested using red water; however, soils and solids contaminated with a variety of organic compounds have been tested using thermal separation technology.
- ° Was the technology evaluated in the 1980 CSL Report? No.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The red water waste stream resulting from production/purification of TNT will be treated.
- ° Is the process a concentrative rather than a treatment effort? No. The technology involves thermal destruction of organic compounds.
- ° Is the treated product suitable for recycle, discharge, disposal, or amenable to further treatment for same? Yes. Off-gas from the separator can be treated by fume incineration or by condensation/scrubbing. Condensed water and organics should be treatable by conventional means, such as biological oxidation. Disposal of the solid residue from the thermal separator may be an issue.

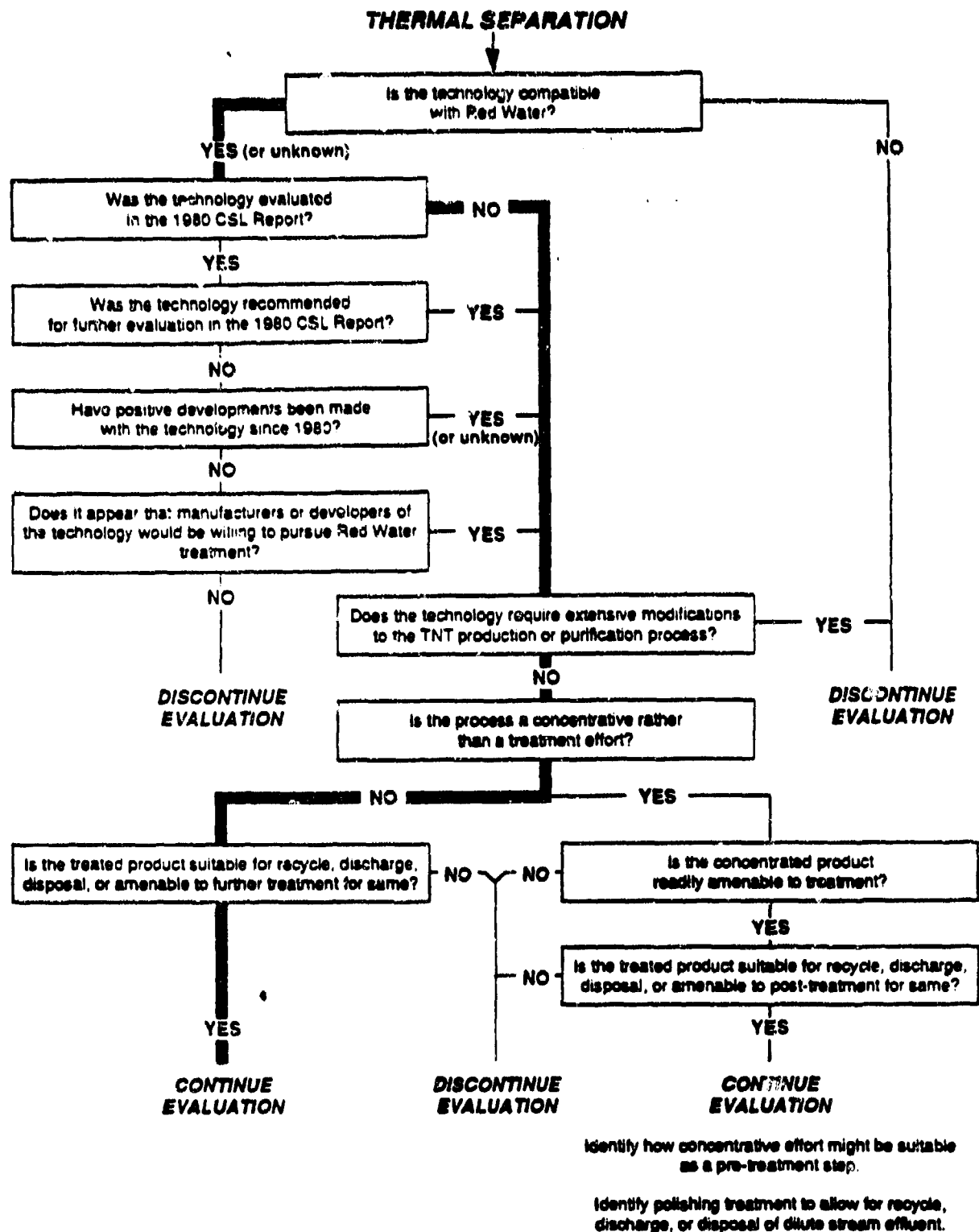


Figure C-10. Prescreening decision tree for thermal separation.

The thermal separation technology has survived the prescreening decision process. Based on the process description and its effectiveness in the destruction of organic compounds, the technology appears to be amenable to treatment of red water at this phase of the evaluation.

AMMONIUM SULFITE PURIFICATION

Ammonium sulfite purification was evaluated in the 1980 CSL report and not recommended for further evaluation. The process involves purifying TNT in a manner similar to the sellite purification process. An aqueous solution of ammonium sulfite $[(\text{NH}_4)_2\text{SO}_3]$ is mixed with the crude TNT in a batch or continuous reactor. Sulfite ions convert the asymmetrical TNT impurities to water-soluble dinitrotoluene sulfonates. The resulting ammonium sulfite red water can be treated by thermal decomposition to ammonia, sulfur dioxide (both of which are easily scrubbed), nitrogen, and water vapor, or alternatively by mixing the waste with denitrated spent sulfuric acid from the nitration process. Sulfur values can then be recovered for use in the purification step. The fate of the dinitrotoluene sulfonates in the red water is not clear.

No commercial applications of this technology currently exist. The initial laboratory development work was conducted at the Picatinny Arsenal in the mid-1970's. Subsequent bench-scale experiments conducted at RAAP have shown that ammonium sulfite is capable of purifying TNT under cold batch processing conditions; however, the higher purification temperature used under continuous processing conditions to maintain TNT in a molten state produces undesirable reaction by-products that impart a bright yellow color and depress the set point of the purified TNT below military specifications. In view of these problems, the 1980 CSL report recommended against further study of ammonium sulfite purification of TNT, although a cost comparison of the technology had not been completed. Subsequent economic analysis showed the capital and operating costs of ammonium sulfite purification to be comparable to those of sellite purification, despite the more conventional red water disposal options.

The decision tree for ammonium sulfite purification is shown in Figure D-1 and the decision tree analysis is provided below:

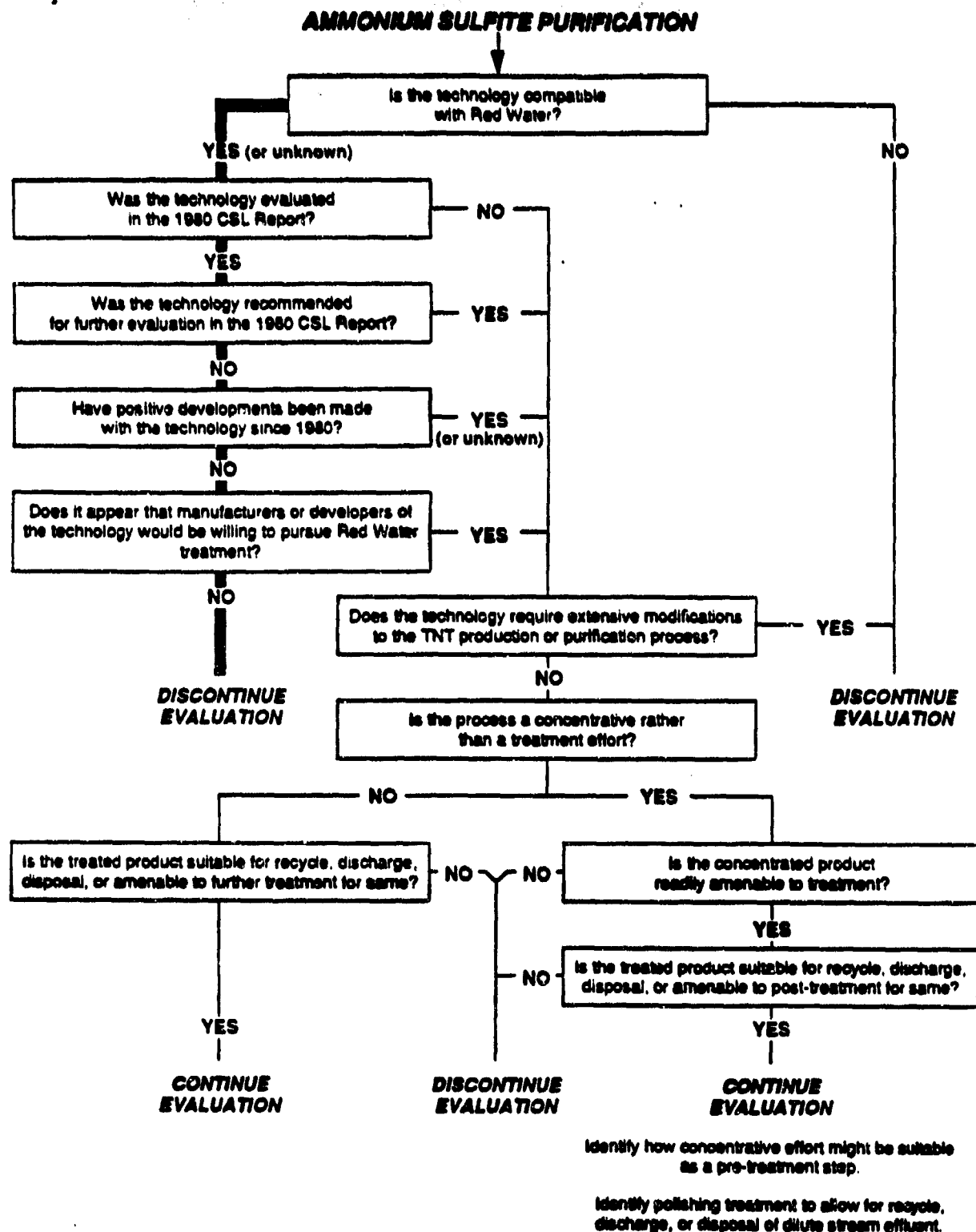


Figure D-1. Prescreening decision tree for ammonium sulfite purification.

- ° Is the technology compatible with red water? Yes. The ammonium sulfite purification process avoids the formation of red water with the characteristics of that produced by the sellite purification process. This is not a treatment technology for red water, but is a process change that would alter the characteristics of the wastewater.
- ° Was the technology evaluated in the 1980 CSL report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? No. The technology was ranked sixth in feasibility in view of the problems discussed above.
- ° Have positive developments been made with the technology since 1980? No.
- ° Does it appear the manufacturers or developers of the technology would be willing to pursue red water treatment? Unknown. The process was patented to E. E. Gilbert at Picatinny Arsenal in 1976. There are no other known manufacturers or developers.
- ° Does the technology require extensive modifications to the TNT production or purification process? Yes. The basis of the technology is to replace the sellite purification process with the ammonium sulfite purification process. Extensive modifications to the process could affect the TNT product performance and all TNT-associated specifications. The high temperature produces undesirable by-products that impart a bright yellow color and depress the set point of the purified TNT below military specifications.

Ammonium sulfite purification is not recommended for further evaluation as a solution to the red water problem.

MAGNESIUM SULFITE PURIFICATION

Magnesium sulfite purification was evaluated in the 1980 CSL report and recommended for further evaluation. The process involves purifying TNT in a manner similar to the sellite purification process. An aqueous solution of magnesium sulfite hexahydrate ($\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$) is mixed with crude TNT in a continuous reactor. Sulfite ions convert the asymmetrical TNT impurities to water-soluble dinitrotoluene sulfonates. The resulting magnesium sulfite red water is then separated from the molten TNT and pumped to a dissolver, where makeup magnesium sulfite, which has a low solubility in water, is continually added to form a saturated solution. The solution is filtered or hydrocycloned to remove solid magnesium sulfite particles that could contaminate the TNT, and the refortified red water is recycled to the purification reactor. The recycling process minimizes the amount of red water that must be treated or disposed. Excess magnesium sulfite red water, which is bled from the recycle stream, can be treated by incineration in a multiple-hearth furnace under reducing conditions (calcination) to form magnesium oxide (MgO). Sulfur dioxide (SO_2) in the combustion gases is then absorbed in the recovered MgO slurry to form MgSO_3 . An analogous recovery process is used in the paper industry to recovery magnesium bisulfite from spent cooking liquor.

The initial laboratory work for this process was conducted at the Picatinny Arsenal and was patented to E. E. Gilbert in 1977. This research demonstrated that improved TNT yields could be obtained with magnesium sulfite purification as compared with sellite purification. For this reason, the 1980 CSL report recommended that the technology be evaluated further. Magnesium sulfite purification was ranked second of the ten processes considered, and was the only one to receive the maximum score for meeting environmental requirements. Subsequent economic analysis showed the capital and operating costs of magnesium sulfite purification to be marginally favorable. Additional bench-scale tests completed in 1981 demonstrated the

feasibility of the red water recycle fortification procedure and the magnesium sulfite recovery process; however, no pilot-scale tests have been conducted.

The prescreening decision tree for magnesium sulfite purification is shown in Figure D-2 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Yes. The magnesium sulfite purification process is not a treatment technology for red water, but is a process change that would alter the characteristics of the wastewater. The recycle loop would also minimize the quantity of red water generated.
- ° Was the technology evaluated in the 1980 CSL report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? Yes. Magnesium sulfite purification was ranked second of the 10 technologies and received high scores for cost and meeting environmental requirements.
- ° Does the technology require extensive modifications to the TNT production or purification process? Yes. The basis of the technology is to replace the sellite purification process with the magnesium sulfite purification process. Extensive modifications to the process could affect the TNT product performance and all TNT-associated specifications.

Because magnesium sulfite purification involves changing the TNT purification process, this technology is not recommended for further evaluation as a solution to the red water problem.

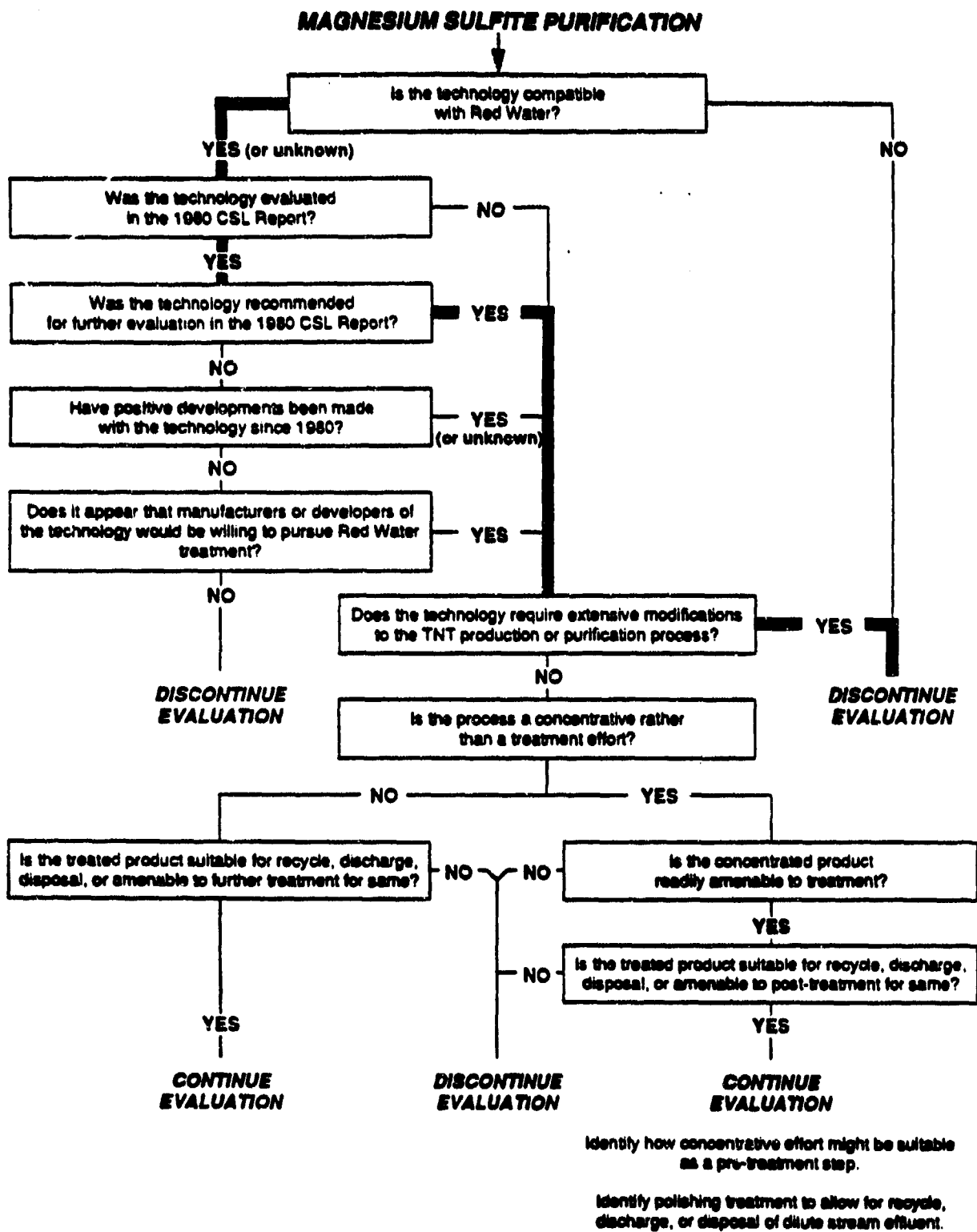


Figure D-2. Prescreening decision tree for magnesium sulfite purification.

NITRIC ACID PURIFICATION

Nitric acid purification is another method for avoiding the production of red water from the TNT sellite purification process. The process was evaluated in the 1980 CSL report and recommended for further evaluation. Two nitric acid recrystallization processes are currently used in Europe for TNT purification. In the Bofors process, which was developed in Sweden, crude TNT from the nitration plant is washed with 50 percent nitric acid to remove any remaining sulfuric acid. The washed crude is then mixed with an approximately equal weight of 60 percent hot nitric acid for removal of all impurities (asymmetrical isomers of TNT, DNT, and oxidation products), which appear as an oil layer. The mixture is cooled to crystallize pure TNT, which is then filtered, washed with nitric acid and hot water, dried, and flaked. In the Leonard process, which was developed in the United States, sufficient hot nitric acid is used to totally dissolve the crude TNT and crystallize out only 2,4,6-TNT by cooling.

The liquid from the screening operation is feed to a falling film evaporator where nitric acid vapor is condensed and recycled to the purification process. The column bottoms consist of approximately 50 percent TNT impurities and 50 percent 2,4,6-TNT. This material, called isotriol, is washed with water and a sodium carbonate solution, and then dried. A method has been proposed to recover two-thirds of the 2,4,6-TNT by feeding the isotriol to a Brodie purifier, which is a device that establishes an equilibrium between liquid and solid phases, thus allowing separation. Remaining material can then be incinerated.

The nitric acid purification process produces TNT-contaminated wastewater, which could be treated by carbon adsorption. Isotriol is a more complicated disposal problem. Possible solutions include sale to the civilian munitions market, incineration (which could create air emissions

problems), chemical alteration, or fractional crystallization. Tetranitromethane (TNM) gas is also produced, and EPA prohibits its discharge to the atmosphere.

The process was ranked third in the 1980 CSL report and recommended for further study. The purification step is fully developed, but further work would need to be done on the disposal of isotriol and destruction of TNM.

The decision tree for nitric acid purification is shown in Figure D-3 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Yes. The nitric acid purification process is not a treatment technology for red water, but is a process change that would alter the characteristics of the wastewater. Wash water is recycled and TNT-contaminated wastewater is more amenable to common treatment methods than is red water.
- ° Was the technology evaluated in the 1980 CSL report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? Yes. Nitric acid purification was ranked third out of the ten technologies studied, receiving high scores for status of development and commercial applications.
- ° Does the technology require extensive modifications to the TNT production or purification process? Yes. The basis of the technology is to replace the sellite purification process with the nitric acid purification process. The 1980 CSL report noted that TNT purified by the process is too pure, which makes the product brittle and more susceptible to cracking in the filled munition, but that this problem could perhaps be overcome by controlling the conditions of recrystallization. Extensive modifications to the process could affect the TNT product performance and all TNT-associated specification, which would require extensive testing to implement for military use.

Because nitric acid purification involves making changes to the TNT purification process, this technology is not recommended for further evaluation as a solution to the red water problem.

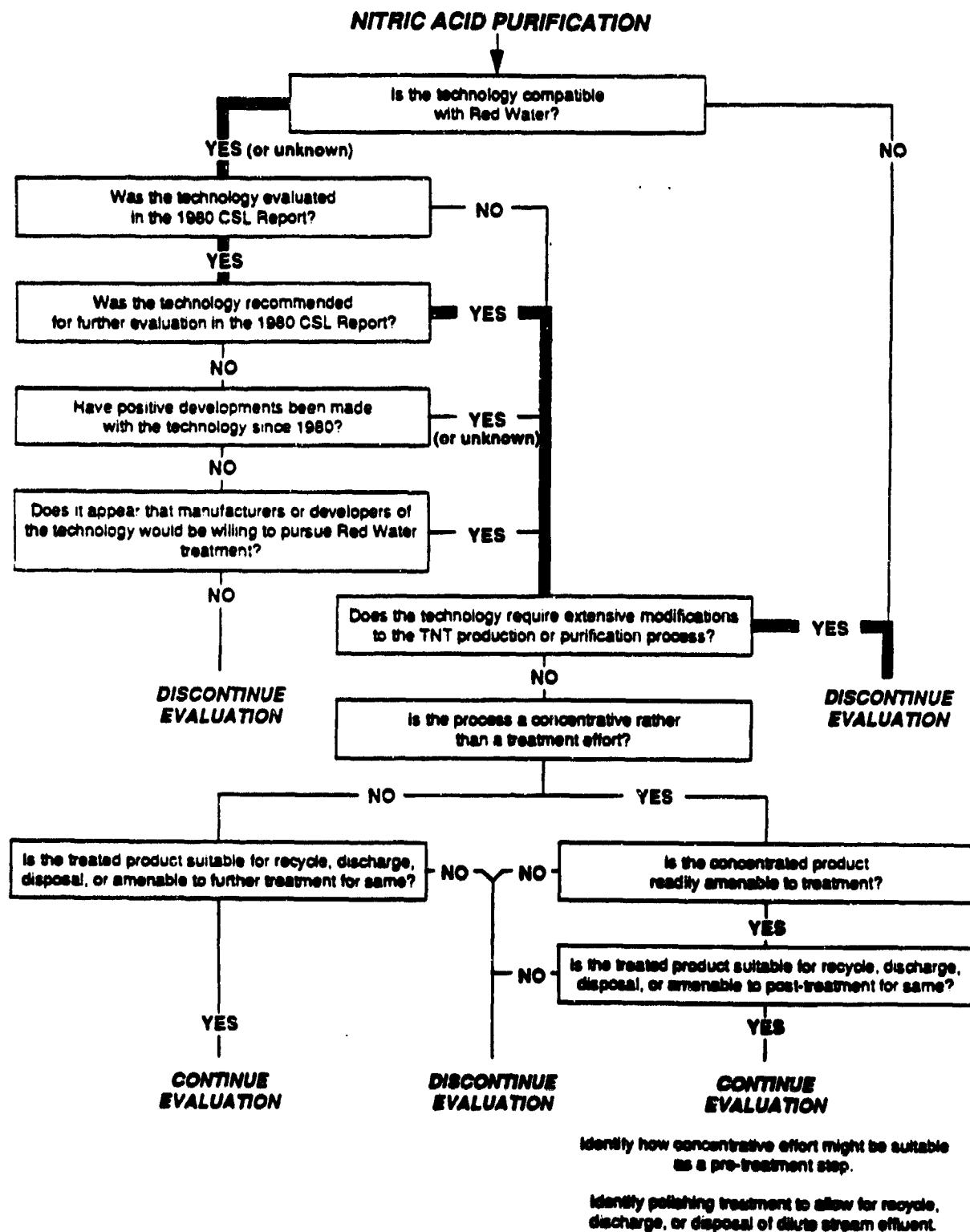


Figure D-3. Prescreening decision tree for nitric acid purification.

ARGONNE NATIONAL LABORATORY PROCESS

Dr. Norman Sather of Argonne National Laboratory (ANL) has proposed a process for the treatment of red water resulting from TNT production. The process is purely conceptual and, at this time, there has been neither laboratory nor pilot plant work validating the process. Consequently, the answer to many of the questions in the decision tree analysis is "unknown". Therefore, the decision tree does not produce an unequivocal answer to the question as to whether evaluation of the process should continue.

The ANL process has six steps:

- ° Foam fractionation to separate the inorganic and organic components.
- ° Biotreatment of the organic wastes.
- ° Solvent extraction of the inorganic waste to form sodium sulfite.
- ° Carbon adsorption of the organic and inorganic wastes from the solvent extraction step.
- ° Evaporation and drying of the remaining untreated wastes.
- ° Recycle of the wastes back into the TNT process.

The first two steps are critical and are the backbone of the process. According to Dr. Sather, the solvent extraction step depends upon the economics of sodium sulfite recovery and his attention is focused upon the first two steps (Sather, 1989). Dr. Sather will not deal with the rest of the technology until the first two steps have been validated.

Dr. Sather proposed foam fractionation as a means of separating the organic and inorganic constituents of red water. In the ANL red water treatment process, foam fractionation concentrates dissolved organic compounds by adsorption in foam. Nelson J. Nemerow reports a 50 to 75 percent reduction in alkyl benzene sulfonate concentrations by a single stage foam fractionation

and indicates that pH control of the wastewater is critical (Nemerow, 1971). According to Dr. Sather, alkyl benzene sulfonate separation occurs at a pH of two to three. Since almost total organic compounds removal would be required, Dr. Sather suggested a 10 to 15 stage continuous operation. If each stage achieved a 50 percent beneficiation, ten stages would reduce the organic concentration to 0.1 percent of the original level. This would require ten successive stages of foam formation, foam separation, and foam breaking, in a first step of some complexity.

Dr. Sather pointed out that alkyl benzene sulfonates are extensively used in detergents as surfactants and by analogy the dinitrotoluene sulfonates found in red water should also have surfactant properties and should be amenable to foam fractionation. As verification of this, Dr. Sather pointed out that red water foams.

Successful surface-active agents have both polar and non-polar attributes. A soap is the sodium salt of a long chain fatty acid such as oleic acid. The carboxylate anion is polar and is compatible with the aqueous phase. The carbon chain is non-polar and is compatible with oils and greases. In alkyl benzene sulfates, the benzene sulfonate anion is polar and the alkyl group is non-polar. The dinitrobenzene sulfonates found in red water lack the non-polar entity. Foam separation for red water sulfonates may be less efficient than anticipated.

In addition, alkyl benzene sulfonate foam fractionation takes place at a pH of two to three. This suggests that the non-ionized alkyl benzene sulfonate acid is the species adsorbed on the foam. Benzene sulfonic acid is a moderately strong acid (the ionization constant is 0.2 compared to 1.8×10^{-5} for acetic acid). Based upon ionization constants of long chain fatty acids, alkyl benzene sulfonic acids will have ionization constants of the same order of magnitude. However, nitro groups on a benzene ring enhance the acidity of an aromatic acid and it would require a much lower pH to produce the non-ionized acid molecule. Phenol provides an illustration:

<u>Phenol</u>	<u>Ionization constant</u>
Phenol	1.28×10^{-10}
Orthonitrophenol	6.8×10^{-8}
Metanitrophenol	5.3×10^{-9}

<u>Phenol</u>	<u>Ionization constant</u>
Paranitrophenol	7×10^{-8}
2,4-dinitrophenol	1.1×10^{-4}
Picric acid (2,4,6 trinitrophenol)	0.42

Since the ionization constant of benzene sulfonic acid is 0.2, adding two nitro groups to the benzene ring will produce a strong acid approaching the strength of the mineral inorganic acids such as hydrochloric, nitric, and sulfuric acids. The separation efficiency by foam fractionation of dinitrobenzene sulfonic acids may be unacceptably low. If acidification to a pH of zero or one is necessary for fractionation, this acid will eventually have to be neutralized as part of the waste treatment process. This will add to the dissolved salt content of the wastewater. Dr. Sather has collected bacteria and enzymes that he intends to test on red water. Industry has developed microbiological species that degrade wastewater from dinitrotoluene (DNT) production. These species could conceivably degrade wastewater from TNT production. However, the DNT production facilities make other chemicals so that nitro compounds make up only a fraction of the organic loading to the wastewater treatment facility. Interviews with industrial representatives indicate that microbiological degradation of nitro compounds is accomplished more effectively when the nitro compounds are diluted with other organic matter.

The Radford AAP red water is about eight percent organic matter with practically all of this being nitro compounds. Foam fractionation could conceivably further concentrate the nitro compounds prior to bacterial oxidation.

A massive trial-and-error effort has recently been initiated to identify an optimum combination of bacteria, fungi, and enzymes to achieve ring cleavage. In Phase I, which began in late February, the bench-scale studies are being conducted in test tubes. A quick screening method will be used to discover evidence of ring cleavage. Selection of a process configuration will be postponed until the precise combination of microorganisms is identified. At this point, no particular biotreatment process is ready for evaluation.

Even if a suitable microorganism is found, several process parameters will have to be defined. These will include residence times in settling tanks, aeration ponds, and the sludge digestors (microbiological oxidation). Biological sludge disposal may be a serious problem. The wastewater after biological treatment may not meet water discharge standards and may require additional treatment. Developing a biological treatment system for aromatic nitro compounds will require a major effort.

Dr. Sather proposes recovering and recycling sodium sulfite through a solvent extraction process. Solvent extraction technology applications are usually limited to products costing dollars per pound such as uranium and specialty organic compounds. One exception is boric acid, which costs \$658 per ton. When the boric acid extraction process was introduced in 1963, boric acid sold for \$100 per ton. The process was considered to be a major breakthrough in the application of solvent extraction technology to a low-cost product. At this time, the plant was marginally profitable but it is now profitable since boric acid prices have risen faster than inflation and the plant is fully depreciated. Sodium sulfite now sells for \$90 a ton and an economic solvent extraction process for sodium sulfite recovery would represent an extension of solvent extraction technology (chemical prices are from the January 30, 1989 Chemical Marketing Reporter). The recovery of sodium sulfite would have to be part of a treatment process to hope to be economical.

In the development of a process, economically acceptable parameters would have to be defined for:

- ° Sodium sulfite distribution coefficients for the organic and aqueous phases.
- ° The organic to aqueous volume ratio for each extraction stage.
- ° The number of extraction stages required.
- ° Stripping extracted material from the organic phase.
- ° Holding organic phase losses by entrainment, evaporation, and solution in the aqueous phase to economically acceptable levels.
- ° Producing a wastewater suitable for either discharge or treatment.
- ° Breaking or avoiding the formation of emulsions.

Activated carbon removal of color bodies from wastewater is established industrial practices for DNT production and may be feasible as the fourth step in the ANL process.

A potential problem in drying solids was pointed out by Glenn Halsey of DuPont. Mr. Halsey said that solids for dinitrotoluene manufacturing can explode on being dried. A similar hazard could be expected when drying solids from TNT manufacturing. The hazard would be more likely to manifest itself on plant or large pilot plant scale when heat transfer was less uniform than in laboratory scale work.

Water recycling to the TNT manufacturing process would be desirable but as long as a wastewater can be produced that is suitable for discharge, water recycling would not be a mandatory part of the process.

We discussed the ANL process with James Carrazza of the U.S. Army Research and Development Center (ARDEC), in Dover, New Jersey. Mr. Carrazza observed that the process is very complex and much of the technology is unproven. He concluded that the process will probably be proven inviable and that the four year development schedule and the process uncertainties make mandatory the evaluation and investigation of alternative technologies.

For the ANL process to become a viable technology, success has to be demonstrated both on small scale (laboratory and pilot plant) and plant scale levels. ANL's process development schedule is four years. It is very possible that the process may eventually be shown to be technically and/or economically unacceptable.

The decision tree for the ANL process is shown in Figure E-1 and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Unknown. There has been no laboratory testing with red water.
- ° Was the technology evaluated in the 1980 CSL report? No. The process was developed after 1980.
- ° Would the manufacturer of the technology be willing to pursue red water treatment? Yes. Dr. Sather plans to use Canadian red water for the testing program.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. The recycle of water and sodium sulfite is proposed but this is not required by the technology.

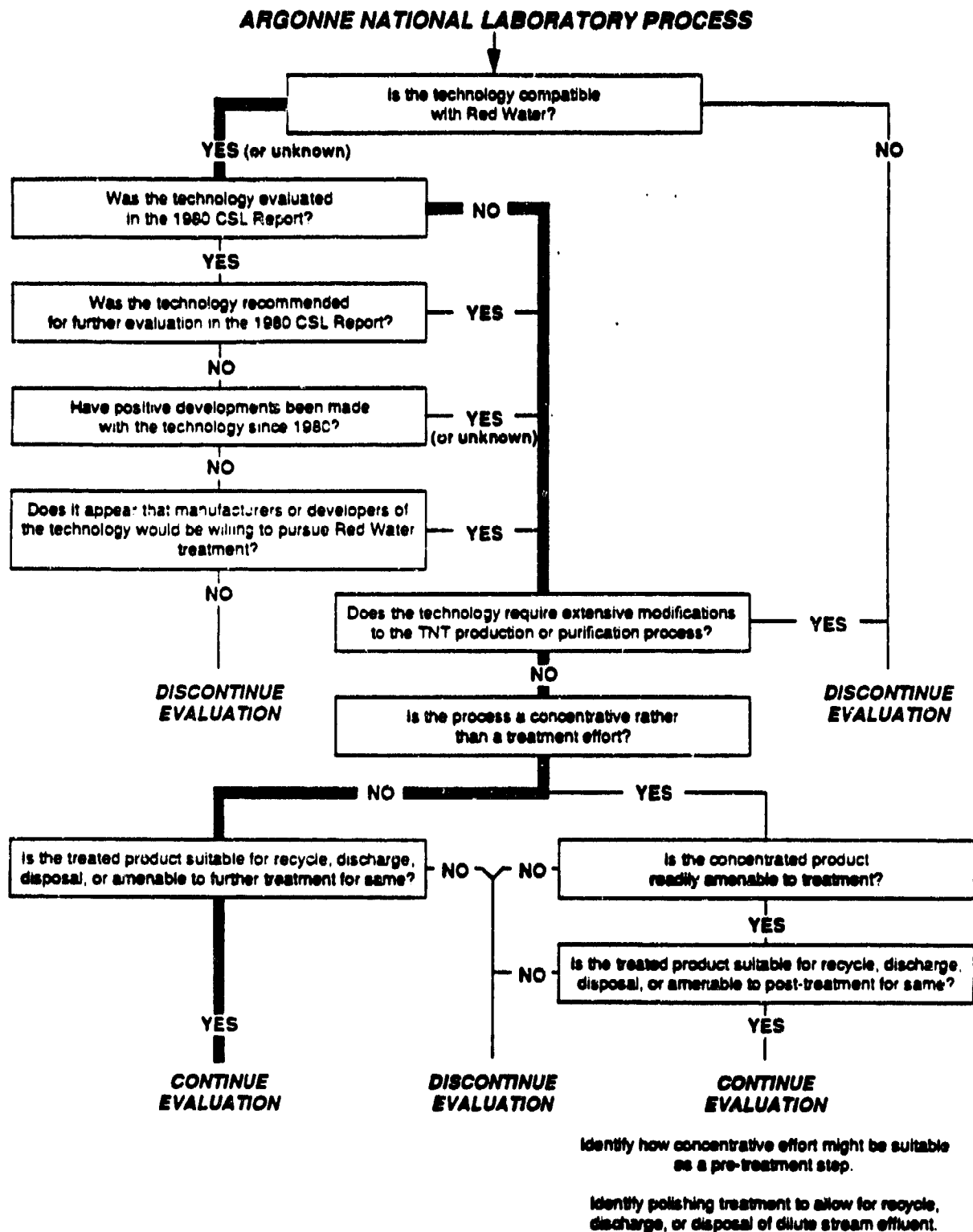


Figure E-1. Prescreening decision tree for the Argonne National Laboratory process.

- Is the process a concentrative effort? No.
- Are the treated products suitable for recycle, discharge, disposal, or amenable to post treatment for same? Unknown. Establishing this is a major part of the ANL R&D effort.

If all of the unknowns are satisfactorily resolved, the ANL process is viable and should be further evaluated. However, by ANL's schedule, definitive answers are four years away. Consequently, progress should be monitored but a secondary evaluation may not be possible until more information is available.

LICENSING EXISTING INDUSTRIAL TECHNOLOGY

Dinitrotoluene (DNT) manufacturers treat their process wastewater using proprietary technology. They are able to satisfy applicable wastewater discharge regulations. DuPont and Air Products and Chemicals Company have expressed an interest in licensing their technologies to the U.S. Army. Dupont has also expressed an interest in treating TNT red water at the Deepwater, New Jersey, wastewater treatment facility.

If technology were licensed, steps in the program would be:

- ° Laboratory bench-scale and/or pilot plant-scale testing of TNT red water.
- ° Full scale testing in the company's wastewater treatment facility.
- ° Engineering, design, and construction of a wastewater treatment facility on the army ammunition plant site.
- ° Start-up and operation of the on-site wastewater treatment facility.

Shipping red water to DuPont's Deepwater, New Jersey, wastewater treatment facility would still require the first two steps but would avoid the third and fourth steps.

If successful, licensing existing technology could have the advantages of a quicker solution to the TNT red water disposal problem at a lower cost than for developing new technology.

Air Products and Chemicals manufactures dinitrotoluene. The wastewater is treated with hydrogen peroxide followed by an iron ferrocene catalyst to break the benzene ring. After biological treatment, the effluent is sent to a cooperative facility where it undergoes a large amount of dilution. The effluent from this facility is polished with activated carbon to remove color bodies. Air Products and Chemicals is conducting research to enhance the activation of carbon.

DuPont representatives have offered to investigate the feasibility of treating TNT red water at DuPont's Deepwater, New Jersey, wastewater treatment facility. The facility is licensed to accept K047 wastes (wastes from TNT manufacturing). DuPont has had sufficient experience in DNT and explosives manufacturing that the willingness to consider taking red water indicates that success is a distinct possibility.

Sending the wastes to Deepwater would have the following advantages:

- ° The question of feasibility would be answered quickly, leaving the options open of exploring other technologies.
- ° Deepwater is already permitted to accept K047 wastes. The Army would not have the effort, expense, and time loss of obtaining discharge permits.
- ° TNT red water would be mixed with other organic chemical wastes. This may render red water more amenable to treatment.
- ° The Deepwater wastewater treatment facility is much larger than the on-site wastewater treatment facility would be at an Army Ammunition plant. Economies of scale may render treatment costs lower than those for a captive facility even after paying rail freight to Deepwater (the Radford Plant would generate about one tank car per day of red water).
- ° Shipping red water directly to Deepwater could avoid complications resulting from DuPont's having to divulge proprietary technologies to the contractor operating the Army ammunition plant. DuPont might consider the contractor a competitor and be reluctant to divulge proprietary technology to either the Army or the contractor.

Areas requiring further investigation are:

- ° The licensing and protection of proprietary technology could create problems, particularly if the ammunition plant is operated by a contractor that DuPont or Air Products consider to be a competitor.
- ° DNT "red water" and TNT "red water" have different organic and inorganic compounds present and TNT red water may not be treatable in facilities designed and built to treat DNT red water. It is not clear if sulfonates could be effectively treated.
- ° DNT red water contains organic chemical compounds from chemical processing other than nitration. Thus, organic compounds are present other than nitro compounds. All of the organic compounds present in TNT red water in significant amounts have at least two

nitro groups on a benzene ring. The dilution of nitro compounds with other organic compounds may make DNT red water easier to biodegrade. A system where all organic compounds have been nitrated may be difficult to degrade.

Even if TNT is treatable, process parameters such as residence times in settling tanks, aeration basins, and biological treatment ponds, pH control, temperature control, etc., may be sufficiently different from operating parameters for treating DNT red water that much more process development effort may be required than anticipated.

With these caveats in mind, licensing existing technology has sufficient promise that follow-up efforts are in order.

DuPont and Air Product's initiation of the discussions of licensing technology indicate that they feel that the problems are solvable. It may be possible to address these caveats fairly quickly, especially with the option of shipping the red water to an existing plant.

The decision tree for licensing existing technology is shown in Figure D-2 and the decision tree analysis is provided below:

- Is the technology compatible with red water? Unknown. It is compatible with DNT red water but has not been tested with TNT red water.
- Was the technology evaluated in the 1980 CSL report? No.
- Does the technology require extensive modifications to the TNT production or purification process? No. All discussions with DuPont and Air Products have been based on red water after it leaves the TNT purification process.
- Is the process a concentrative effort? No. The technology is wastewater treatment yielding water suitable for discharge.
- Is the treated product suitable for recycle, discharge, or disposal or amenable to further treatment? Yes. The processing, when applied to DNT red water, produces a water suitable for discharge that complies with all applicable regulations and standards.

This red water treatment method has sufficient potential cost and timing advantages that it should be actively investigated.

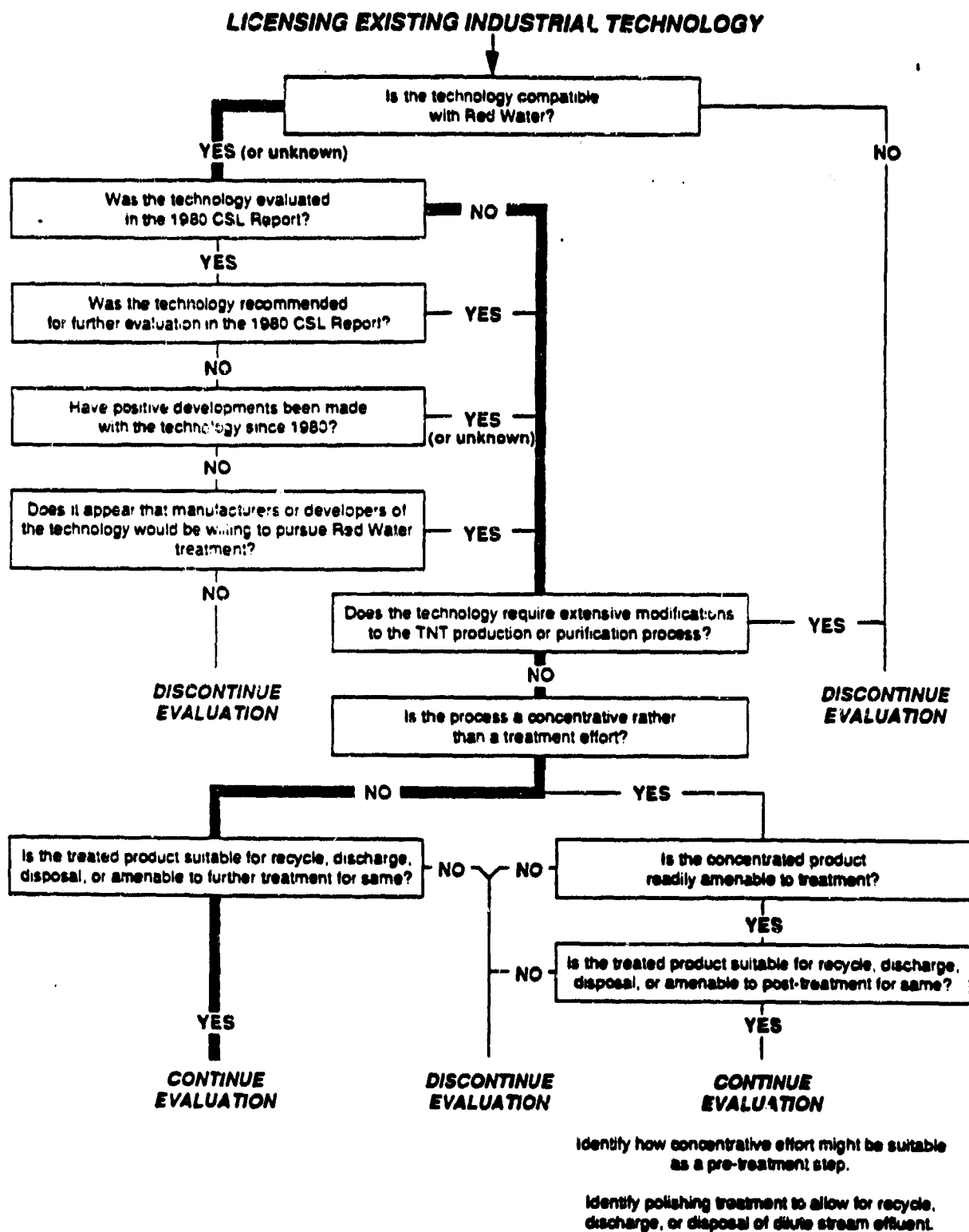


Figure E-2. Prescreening decision tree for licensing existing industrial technology.

SONOCO SULFITE RECOVERY PROCESS

The Sonoco sulfite recovery process has been used in the paper industry to recovery sulfite from spent black liquors. Applied to red water, the process would recover sellite from red water in a closed-loop recycle system. The sellite can then be recycled back to the TNT purification process.

In the Sonoco sulfite recovery process, red water is first concentrated to 35 percent solids in a multiple effects evaporator. The liquid is then mixed with filter cake in a repulper section of a belt filter to obtain a 36 percent solids solution, after which it is concentrated to 68 percent solids in a hollow shaft evaporator. The resulting material is mixed with recycled furnace ash and petroleum coke to a 74 percent solids concentration and fed to a multiple hearth furnace. The top six hearths of the furnace are a reducing zone, forming an ash $[\text{NaAlO}_2]$ and sodium sulfide (Na_2S). The bottom two hearths oxidize the ash to form NaAlO_2 and sodium sulfate (Na_2SO_4). Flue gases from the furnace pass through an afterburner where hydrogen sulfide (H_2S) is oxidized to sulfur dioxide (SO_2) and water (H_2O). A Schneible scrubber absorbs the SO_2 and converts sodium sulfite (Na_2SO_3) into sodium bisulfite (NaHSO_3). The sodium bisulfite is treated in a precipitator with furnace ash (NaAlO_2) to precipitate aluminum hydroxide $[\text{Al}(\text{OH})_3]$ and form sellite (Na_2SO_3). A solid bowl centrifuge separates the aluminum hydroxide from the sellite solution, which can then be recycled to the TNT purification process.

Construction of a sulfite recovery process was begun at the Radford Army Ammunition Plant (RAAP) but has been halted. Pilot tests concentrating on safely feeding the red water to the furnace were successfully completed prior to beginning construction on the facility. Several problems have arisen concerning adapting the Sonoco process to red water treatment at RAAP. Several equipment modifications to address these problems have been proposed. Additional studies would need to be conducted to test these modifications.

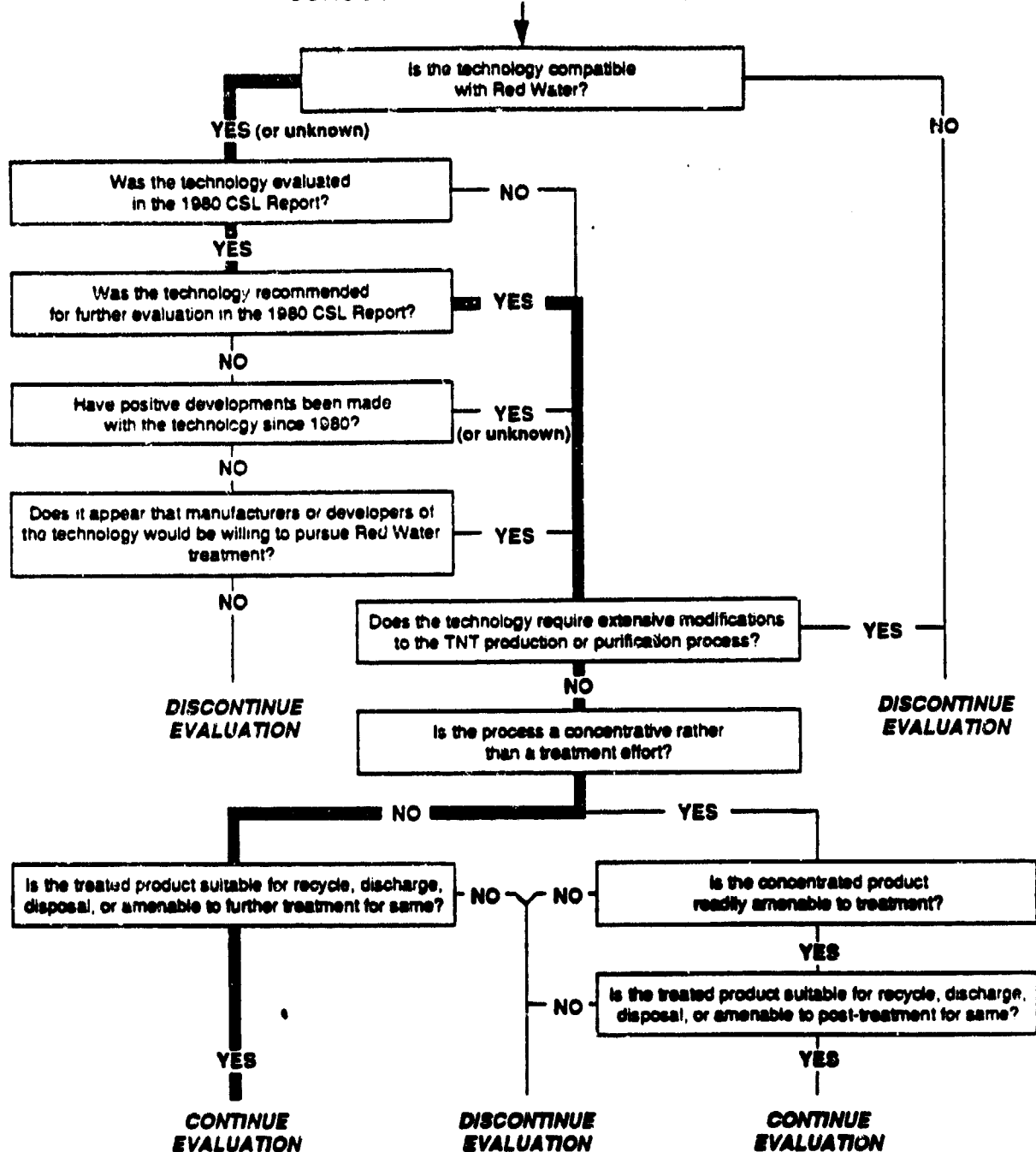
It is currently unknown if the ash produced in the multiple hearth furnace will contribute impurities to the sellite in high enough concentrations to affect the TNT purification process. It is also unknown what quantity of nitrous oxides (NO_x) will be formed in the afterburner, and if the NO_x formed will be controlled by the scrubber.

The prescreening decision tree for the Sonoco sulfite recovery process is shown in Figure F-3, and the decision tree analysis is provided below:

- ° Is the technology compatible with red water? Yes. Pilot-scale studies have indicated that the Sonoco sulfite recovery process is compatible with red water. However, more thorough testing with red water needs to be completed.
- ° Was the technology evaluated in the 1980 CSL report? Yes.
- ° Was the technology recommended for further evaluation in the 1980 CSL report? Yes. Of the ten processes studied, the Sonoco sulfite recovery process was judged to be the best suited for adaptation to red water treatment.
- ° Have positive developments been made with the technology since 1980? Yes. Most developments have involved paper evaluations only since the construction at RAAP has been stopped. However, the evaluations have been positive.
- ° Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? Yes. The Sonoco manufacturers are willing to help in sorting out the adaptation of the process to red water treatment.
- ° Does the technology require extensive modifications to the TNT production or purification process? No. However, the recovered sulfite could be recycled to the purification process. It is currently unknown if the ash produced in the multiple hearth furnace will contribute impurities to the sellite in high enough concentrations to affect the TNT purification step.
- ° Is the process a concentrative effort rather than a treatment effort? No. The red water is converted into sellite.
- ° Is the treated product suitable for recycle, discharge or disposal, or amenable to further treatment for the same? Yes. The product (sellite) may be suitable for recycle into the TNT purification process. However, it is unknown if impurities in the sellite will affect this process.

The Sonoco sulfite recovery process has survived the go/no-go decision tree and is recommended for further evaluation.

SONOCO SULFITE RECOVERY PROCESS



Identify how concentrative effort might be suitable as a pre-treatment step.

Identify polishing treatment to allow for recycle, discharge, or disposal of dilute stream effluent.

Figure E-3. Prescreening decision tree for Sonoco sulfite recovery process.

REFERENCES FOR PRELIMINARY SCREENING

Adams, Michael (Rohm and Haas). 1989. Personal communication.

Albright, Robert, and Peter Yarnell (Rohm and Haas). Encyclopedia of Polymer Science and Engineering, 2nd ed.

Applegate, Lynn (DuPont). Membrane Separation Processes. Chemical Engineering, June 11, 1985.

Carazza, James. (ARDEC). 1989. Personal communication.

Combustion Engineering, Inc. 1986. Raymond Rotary Incineration Systems. 865R2. Solutions for Hazardous and Toxic Waste Disposal.

Combustion Engineering. 1989. Personal communication.

Connor, Jesse (Chemical Waste Management). 1989. Personal communication.

Copa, William M. (Zimpro/Passavant, Vice President of Technical and Field Services). 1989. Personal communication.

Devin, R. (Combustion Engineering, Inc.). 1989. Personal communication

Dogonaglu, Y. (Canadian Industries Limited, Toronto, Canada). 1989. Personal communication.

DuVall, Edward W. (AVCO Corporation), James H. Fraser (Concentration Specialists, Inc.), and Edward Pregon (U.S. Army Armament Research and Development Command). Feasibility Tests and Economic Study of Concentrating Red Water with a Two Stage Freezing Process. Contractor Report ARLCD-CR-78028. June 1970.

Eckenrode, J., G. Densler, and J. Klein. (Environmental Technology Division, Chemical Systems Laboratory, U.S. Army Armament Research and Development Command). Technical Report ARCSL-TR-90023. Evaluation of TNT Red Water Pollution Abatement Technologies, Final Report. April 1980.

Evans, Bill. White Rot Fungus Fights Toxic Waste. Mechanical Engineering, February 1989.

Ford, Bacon, and Davis. 1989. Personal communication.

Foster Wheeler. Final Report on Treatment of TNT Thick Liquor. June 15, 1988.

REFERENCES FOR PRELIMINARY SCREENING (continued)

Fox, R. 1968. International Technology Corporation (IT) Memorandum on Alternative Technologies for Red Water Treatment. Knoxville, TN.

Freeman, Donald J. (ARDEC). Continuous Fixation and Removal of Explosive Wastes from Pink Water Using Surfactant Technology, in Proceedings of the Purdue University Industrial Waste Conference. 1985.

Gilbert, Everett (ARDEC). 1989. Personal communication.

Glaser, J. Use of White Rot Fungus in a Rotating Biological Contactor. Presented at the AWMA/EPA Bioremediation Symposium, Cincinnati, Ohio, February 21-23, 1989.

Hinshaw, G. D., Fanska, C. B., Fiscus, D. E., and Sorensen, S. A. Granular Activated Carbon (GAC) System Performance Capabilities and Optimization. Midwest Research Institute, USATHAMA, February 1987.

International Technology Corporation (IT). n.d. Brochure: On-Site Treatment. Transportable Hybrid Thermal Treatment System, Knoxville, TN.

Joyce, Thomas (North Carolina State University). 1989. Personal communication.

Joyce, Thomas, H. Chang, B. Vasudevan, H. Taneda (North Carolina State University). Degradation of Hazardous Organics by the White Rot Fungus Phanerochaete Chrysosporium. Presented to the Division of Environmental Chemistry, American Chemical Society, New Orleans, Louisiana. August 30 - September 4, 1987.

Kutuoglu, E. (Canadian Industries Limited, Toronto, Canada). 1989. Personal communication.

Lummus Crest Company. 1989. Personal communication.

Nemerow, Nelson L. 1971. Liquid Waste of Industry, Theories, Practices, and Treatment. Addison-Wesley Publishing Company, 1971, page 129.

Okamoto, Y. et. al. (Polytechnic Institute of New York), Freeman, D. et al. (ARRADCOM). Removal of 2,4,6-Trinitrotoluene (TNT) and 1,3,5-Trinitro-1,3,5-Triazacyclohexane (RDX) from Aqueous Solution with Surfactants. Propellants, Explosives, Pyrotechnics 7, 18-21 (1982).

Rosenblatt, David H. Investigations Related to Prevention and Control of Water Pollution in the U.S. TNT Industry, in Proceedings of the 1st International Meeting of the Society of Engineering Science, Tel Aviv, 1972.

Sather, Norman (Argonne National Laboratory). 1989. Personal communication.

REFERENCES FOR PRELIMINARY SCREENING (continued)

Schott, S. I., Ruchhoft, C. G., and Megregian, S. "TNT Wastes". Industrial Engineering Chemistry, 35:10:1122, October 1943.

Schulte, G. R., Hoehn, R. C., and Randall, C. W. The Treatability of a Munitions-Manufacturing Waste with Activated Carbon, in Proceedings of the 28th Purdue Industrial Waste Conference. Purdue University. W. Lafayette, Indiana. May 2-4, 1973.

Shell, C. (International Technology Corporation, Knoxville, TN). 1989. Personal communication.

Siciu, Daniel (CE Environmental, Inc.). 1989. Personal communication.

Warner, David (DuPont). 1989. Personal communication.

Weston, Roy F. Task Order 8: Field Demonstration - Composting of Explosives- Contaminated Sediments at the Louisiana Army Ammunition Plant (LAAP); Contract No. DAAK-11-85-D-007; Report No. AMXTH-IT-TE-86242. September 1988.

APPENDIX D
DETAILED EVALUATIONS OF POTENTIAL
RED WATER TREATMENT TECHNOLOGIES

CONTENTS

<u>Technology</u>	<u>Page</u>
Biodegradation by White Rot Fungus on a Packed-Bed Reactor	D-2
Catalyzed Wet Oxidation	D-6
Liquid-Phase Oxidation	D-13
Solids Precipitation With Surfactants	D-19
Wet Air Oxidation	D-28
Hybrid Thermal Treatment System (HTTS)	D-36
Plasma Arc	D-43
Slagging Rotary Kiln	D-52
Submerged Combustion Process	D-59
Supercritical Water Oxidation	D-67
Thermal Separation	D-76
Circulating-Bed Combustion	D-83
Sonoco Sulfite Recovery Process (SSRP)	D-89
References for Appendix D	D-107

BIODEGRADATION BY WHITE ROT FUNGUS ON A PACKED-BED REACTOR

TECHNOLOGY DESCRIPTION

The New Jersey Institute of Technology (NJIT) is evaluating a packed-bed reactor configuration for degradation of chlorinated phenols (primarily 2-chlorophenol) by white rot fungus. The packed bed consists of a porous, silica-based, diatomaceous earth that is produced by Manville Remedial in Colorado. Fungi migrate into the 20-micrometer interior of the diatomaceous earth. Columns are 3 feet high and 4 inches wide and operate in an upflow mode with an oxygen sparger at the bottom of the column. This setup provides a surface area-to-volume ratio up to 1000 times higher than that of the rotating biological contactor (RBC). It has no moving parts. Researchers at NJIT are currently working on optimization of oxygen distribution and measurement of enzyme production.

CE Environmental, Inc., has also observed that packed beds have a much higher efficiency than RBCs. In the autumn of 1988, this company switched its research focus to a packed-bed process similar to the one being studied at NJIT.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The theoretical potential of this technology is high. Inasmuch as researchers have observed complete degradation of TNT using an RBC and the packed-bed setup provides a surface area-to-volume ratio up to 1000 times higher than that of the RBC, the theoretical potential of this technology for treating red water is even higher than that for RBCs.

White rot fungus will biodegrade only the organic fraction of the waste stream; it will not remove inorganic salts. At some point in the process stream, either before or after treatment of the waste in the packed-bed reactor (if the presence of these salts does not adversely affect biodegradation), this inorganic fraction must be rerouted for treatment by some other technology.

The one significant qualification to this technology is that it has only been applied to pink water and synthetic pink water. Until it has been demonstrated with actual red water, its success cannot be predicted. The complete effect of the multiple chemical and physical variables, acting alone and in combination, upon the white rot fungus organism is impossible to predict.

Current Application and Status of Technology

Degradation of synthetic pink water and 2-chlorophenol has been demonstrated through the bench scale. At flow rates between 66 and 300 mL/h, contaminant degradation ranged from 97.8 to 100 percent (nondetectable levels). With synthetic pink water (made by dissolving TNT in tap water) in a column with a holding of 170 mL, the best results achieved thus far are as follows:

<u>Flow rate, mL/h</u>	<u>Initial TNT concentration, ppm</u>	<u>Final TNT concentration, ppm</u>
300	1076	24
83	90	Not detectable
66	107	2.4

Because the development of this process is still in the early stages, many questions have not yet been answered and significant uncertainties remain regarding both technical feasibility and process reliability. The extent of these uncertainties, however, is not clear. Bench-scale studies are scheduled to continue at NJIT and CE Environmental.

Environmental Impact

A primary advantage of biodegradation is the complete and permanent mineralization of contaminants into carbon dioxide and water without wastewater discharge, air emissions, or the generation of solid and hazardous wastes. One must keep in mind, however, that the inorganic fraction of the initial waste stream will not be biodegraded and must be treated by an alternate technology.

Until actual red water is tested, whether complete biodegradation of the organic fraction of red water will occur is not known. Partial degradation of the organic fraction of red water will be confirmed by observing certain

metabolic products. These compounds (products of incomplete biological degradation) may or may not be more toxic or persistent than the original contaminants. Theoretically, this technology could produce some wastewater discharge.

Capital and O&M Costs

Cost data (both capital and O&M costs) are not yet available. Estimates would be premature at this time.

Complexity, Operation, and Flexibility

Biological treatment is generally not a complex process from an operational standpoint. The white rot fungus/packed-bed reactor process is relatively simple and should be easy to operate despite any physical or chemical pretreatment steps.

Evaluation Summary

Table D-1 presents a quantitative evaluation of the packed-bed reactor technology based on five categories of evaluation criteria. The final score for biodegradation by white rot fungus on a packed-bed reactor is 51 of a possible 110 points.

TABLE D-1. QUANTITATIVE EVALUATION OF BIODEGRADATION BY
WHITE ROT FUNGUS ON A PACKED-BED REACTOR

	<u>Points awarded</u>	
1. Theoretical potential for red water treatment		8
2. Current application and status of technology		7
3. Environmental impact		17
Wastewater discharge regulations	3	
Air emission regulations	10	
Solid/hazardous waste regulations	4	
Recyclability	0	
4. Time and cost for implementation		6
Time	3	
Cost	3	
5. Complexity, operation, and flexibility		13
Process complexity	3	
Difficulty of operation	4	
Flexibility of operating parameters	3	
Miscellaneous	3	
TOTAL		51

CATALYZED WET OXIDATION

TECHNOLOGY DESCRIPTION

Catalyzed wet oxidation (CWO) is a treatment technology developed by International Technology Corporation (IT) in the 1970s and refined in the early 1980s. The process uses a catalyst system in an acidic aqueous solution to effect the oxidation of organics. Catalysts typically added to the CWO reactor are nitrate (added as nitric acid), bromide (through the addition of hydrogen bromide or bromine gas), and divalent manganese (or some other transitional metal).

Conventional wet oxidation processes use heat and pressure to increase the dissolution of oxygen from air into the liquid phase, where it reacts with dissolved organics. In CWO, a bromide/nitrate/manganese-based catalyst system accelerates the transfer of oxygen to the dissolved state, which results in rapid gas and liquid reactions with the catalyst components. The enhanced oxygen transfer enables organics to be oxidized at much lower temperatures (165° to 250°C versus 250° to 325°C) and lower pressures than in uncatalyzed wet oxidation. This, in turn, reduces capital and operating costs and operational problems (Fox 1988).

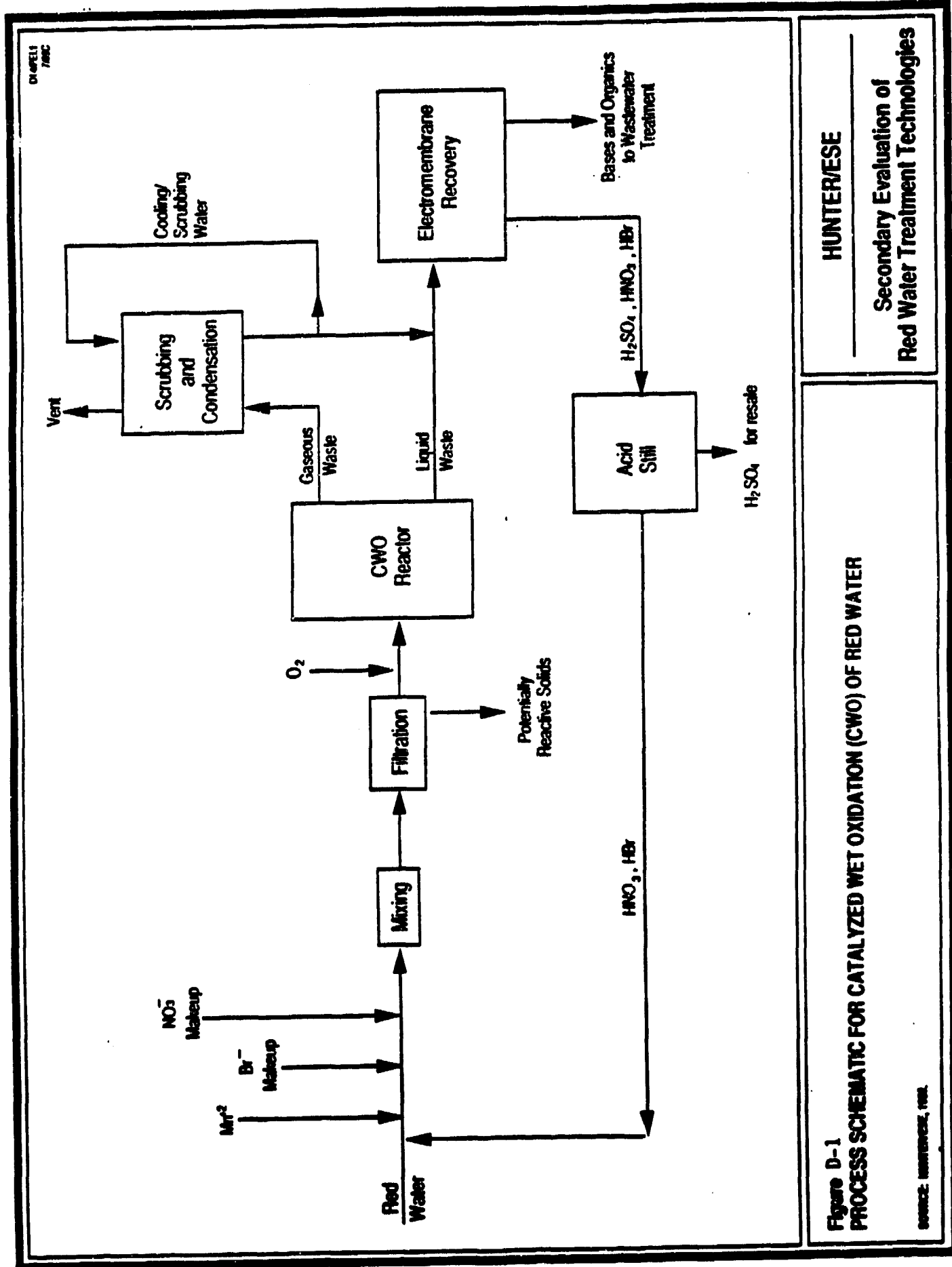
Although this technology has not been tested for treatment of red water, a wide variety of organic compounds have been tested at bench scale in a 1-liter stirred autoclave. The structures of three of these compounds were similar to that of red water, and they contained the following nitro-bodies: nitrobenzene, chloroaniline, and o-xylene. The nitrobenzene CWO experiments were performed at 250°C for 60 minutes. Results of this test revealed that although 46 percent of the nitrobenzene was destroyed, only 12 percent of the original carbon was oxidized to carbon dioxide (CO₂). The remaining 88 percent of the carbon was present in the effluent in the form of various partially oxidized organics and nitro-bodies. Reportedly, the chloroaniline tests indicated rapid oxidation, but quantified results were not available. Byproducts in the reactor effluent included brominated

chlorobenzenes. Tests using o-xylene resulted in 98 percent destruction of the compound; less than half was totally oxidized to CO_2 (Miller and Swientoniewski 1981).

Experiments on the use of CWO have also been performed on a lagoon sediment contaminated with large percentages of TNT, RDX, and tetryl. Water was added to the sediments to form a 10 percent slurry before the waste was added to a 1-liter reaction vessel. The initial TNT concentration was approximately 23 percent (230,000 ppm). For comparison, total nitrobenzenes in the Radford AAP red water are estimated at 85,000 ppm. Results indicated that at 250°C and 90 minutes, 99 percent of the TNT was destroyed; effluent concentrations were 2300 ± 1400 ppm. The RDX and tetryl concentrations were reduced to less than detection limits; however, very little of the carbon contained in these explosives was oxidized to CO_2 (IT Enviroscience 1981). Although these data were not reported, calculations reveal that no more than 20 percent of the carbon was oxidized to CO_2 . The rapid oxidation of RDX and tetryl was similar to that reported by Miller and Swientoniewski (1981) for atrazine. All three of these compounds contain a heterocyclic nitrogen-carbon ring.

Using the CWO process to oxidize red water may require filtration after the addition of catalysts and prior to heating. Pilot studies have revealed that the CWO process is most efficient at a pH considerably less than 4 (Diesen and Moyer 1976). This is the principal reason for adding nitrate and bromide catalysts as nitric acid and hydrogen bromide. The use of acidification in unrelated red water desulfonation testing, however, has resulted in violent explosions. Research revealed that an insoluble compound formed upon acidification was responsible for the explosion. Therefore, filtration may be necessary to remove this compound prior to heating and oxidation (Eckenrode, Densler, and Klein 1980).

Figure D-1 is a process schematic of the treatment of red water with the CWO process. Prior to oxidation, catalyst components (bromide, nitrate, and manganese) would be added to the waste, and the resultant mixture would be filtered for removal of potential insoluble reactive compounds. The waste would then be fed to a CWO reactor system, and sufficient residence time would be allowed to destroy the red water nitrobenzenes as well as partially



HUNTER/USE
Secondary Evaluation of
Red Water Treatment Technologies

oxidized nitrobenzenes. Bench-scale tests would be used to optimize the catalyst composition and time-temperature relationships.

The reactor system can be designed either as a plug-flow tube reactor or as a continuously stirred tank reactor (CSTR). Although a CSTR offers greater reaction control, the feed characteristics and reaction conditions will determine the type of reactor selected.

The reactor would produce two waste streams. One stream, an aqueous effluent, would be organic-free (assuming sufficient detention time is possible) and would contain acidic inorganic salts (sulfates, nitrates, bromides) and other inert solids. This solution would be subjected to a recovery process that involves the use of an electromembrane technology to remove acids from the solution; these acids can then be distilled to recover hydrogen bromide, which leaves a sulfuric-nitric acid mixture that could be recycled for acid recovery. It would still be necessary to dispose of an aqueous waste containing considerable concentrations of partially oxidized organics and nonionic inert materials. The second stream, a gaseous waste stream, would include water vapor, CO_2 , NO_x , SO_2 , and volatile organic compounds that may be formed during oxidation. The water and volatile organics would be condensed for recycling into the CWO reactor. If necessary, the NO_x and SO_2 could be removed through scrubbing (Fox 1988).

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The principal nitrobenzenes found in red water are sulfonated forms of asymmetrical isomers of TNT. These compounds are somewhat similar to several of the compounds used in previous CWO experiments. Although destruction of the original compounds in these tests was documented to various degrees, only limited oxidation to CO_2 was observed in each case where production of CO_2 was monitored. These results suggest that whereas destruction of the sulfonated TNT may occur, the production of partially oxidized nitrobenzenes also occurs during the oxidation process. Because it is somewhat unlikely that discharge of this waste would be acceptable, the theoretical potential of CWO being suitable for treatment of red water is low.

Current Application and Status of Technology

The CWO process has not been tested on red water, but it has been tested on wastes similar to red water. Portions of this process (especially the destruction of the target compound) have been successfully demonstrated in the laboratory.

The technical feasibility of the CWO process represents the principal data gap related to its application. As of now, complete oxidation of the nitrocompounds appears to be unlikely. The process reliability and scale-up capabilities are reasonably well known on a theoretical basis. Because of the apparent lack of full-scale applications of the CWO process, however, reliability and scale-up represent potential problem areas.

Environmental Impact

If the aqueous waste from the CWO process contains the expected significant concentrations of partially oxidized nitrocompounds, this discharge is not likely to comply with wastewater discharge regulations. Scrubbers can be used to remove SO_2 and NO_x from the air emissions to attain compliance with regulations. Few, if any, solid or hazardous wastes will be generated; therefore, no compliance problems are expected. Several constituents of the waste streams will be recyclable; e.g., water vapor can be condensed for reuse, bromide can be recovered for recycling, and nitric and sulfuric acids can be regenerated for recycling. Only the organic compounds in the waste cannot be recycled. As indicated in the following subsection, however, the initial capital cost for a recycling system is considerable.

Time and Cost for Implementation, Capital and O&M Costs

The time involved for laboratory testing, pilot-plant testing, and design to treat red water via the CWO technology has been estimated to be between 12 and 18 months. The cost for testing and development to implementation may range from \$500,000 to \$700,000, depending on the extent of testing performed.

Estimated costs for the operation of a CWO system for oxidation of explosive-contaminated lagoon sediments were presented in a report by IT Enviroscience (1981). These estimates include the costs for catalysts, off-gas scrubbing, and wastewater treatment. No recycling of waste acids

or bromide are considered in these estimates. When these values are updated to 1989 dollars and the figures for the flow rates expected at Radford AAP are revised, the estimated capital cost for installation of the CWO process is \$3 million. Based on these same revisions, O&M costs are estimated to be \$310/1000 gallons.

Costs for the acid and bromide recycling system described earlier were provided by Basta (1986) in a Chemical Engineering article. With appropriate updating and revisions, capital costs are estimated to be \$1.6 to \$2.2 million, and O&M costs are estimated to be \$75/1000 gallons. It is estimated that use of this recycling system would reduce O&M costs for the basic CWO process (through reduced purchases of catalysts) by approximately \$100/1000 gallons. This process should reduce O&M costs by an estimated additional \$50/1000 gallons through the sale of sulfuric acid.

The total capital cost of a CWO process with a catalyst and acid recycling system is therefore estimated to be \$5 million. Total O&M costs are estimated to be \$235/1000 gallons of waste.

Complexity, Operation, and Flexibility

Because of the numerous steps required for CWO operation and waste recycling, the problems of process complexity and difficulty of operation are considerable, but not insurmountable. Operating parameters such as temperature, time, and catalyst concentrations will be somewhat inflexible. Implementation of the CWO process to achieve full-scale operations is not expected to be difficult.

Evaluation Summary

In summary, because of the expected difficulties in oxidizing all nitro-bodies that are initially present in the red water or formed during the oxidation process, the treatment of red water with the CWO process is unlikely to be feasible. Table D-2 presents a quantitative evaluation of CWO based on five categories of evaluation criteria. The final score for the CWO process is 27 of a possible 110 points.

TABLE D-2. QUANTITATIVE EVALUATION OF CATALYZED WET OXIDATION

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	4
2. Current application and status of technology	7
3. Environmental impact	25
Wastewater discharge regulations	2
Air emission regulations	4
Solid/hazardous waste regulations	17
Recyclability	2
4. Time and cost for implementation	6
Time	3
Cost	3
5. Complexity, operation, and flexibility	6
Process complexity	2
Difficulty of operation	1
Flexibility of operating parameters	2
Miscellaneous	1
TOTAL	48

LIQUID-PHASE OXIDATION

TECHNOLOGY DESCRIPTION

Liquid-phase oxidation is accomplished through the use of strong oxidizing agents such as ozone, hydrogen peroxide, and calcium hypochlorite to oxidize aqueous solutions of trinitrotoluene (TNT). The process has been tested with wastewaters containing TNT concentrations of about 100 mg/liter, which approximates those found in pink water. The effectiveness of ozone and hydrogen peroxide has been shown to be enhanced with ultraviolet light, ultrasound, or activated carbon. Table D-3 presents a summary of this work. No studies conducted to date have identified the products of TNT oxidation.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Several obstacles exist for treating red water from a TNT production plant by liquid-phase oxidation. The most serious involves incomplete oxidation, and no effort has been made to identify the oxidation products. For example, Sierka (1985) used ozone and ultrasonic energy to reduce TNT concentrations from 66 mg/liter to 0.6 mg/liter, a 99.1 percent reduction. Total organic carbon, however, was reduced by only 51 percent. Semmens, Barnes, and O'Hara (1985) used hypochlorite oxidation to treat TNT solutions, but made no effort to identify the products. Inasmuch as chlorinated organic compounds are almost always more toxic than the corresponding nonchlorinated compounds, this is a serious omission. Further, residues from treating a RCRA hazardous waste are also defined as hazardous unless specifically delisted.

The most effective ultraviolet wavelength employed is 2540 angstroms, which is the absorption maximum for ozone (Fochtman and Hoff 1975; Burrows 1983). Presumably, ozone absorbs the UV light and the ozone reactivity is enhanced. If, however, any of the organic and inorganic species in solution also absorb UV light at this wavelength, these species would compete with ozone for the UV energy, thereby reducing process efficiency.

TABLE D-3. SUMMARY OF RESULTS OBTAINED BY THE LIQUID PHASE OXIDATION OF TNT SOLUTIONS

Treatment	Scale of work	Description of waste	Results	References
Ozone and ultraviolet light (IT Research Institute)	4-liter reactor	Synthetic pink water with 100 mg/liter of TNT and 2 g/liter of total solids	Total organic carbon (TOC) was reduced from 60 mg/L to 18 mg/L. The reaction stopped after 2 hours. Twelve pounds of ozone were required to oxidize 1 pound of TOC.	Fochtman and Hoff 1975
Ozone with suspended activated carbon	20 to 40 mL/min	TNT levels about 35 mg/liter	Sixty percent reduction of TNT in 40 minutes	Jain 1976
Ozone and ultraviolet light 1983 (U.S. Army Bioengineering R&D Lab, Fort Detrick, Maryland)	6 liters/min	TNT levels about 100 mg/liter	Ultraviolet light and ozone destroyed TNT in solution. May be "suitable for removal of TNT from small process streams (about 20,000 gallons per day).	Burrows
Ozone and ultrasound (University of Arizona)	0.45 cc reactors and 1-liter	Synthetic TNT and RDX solutions, 70 mg/liter of TNT, 30 mg/liter of RDX.	Achieved 99 percent destruction of TNT in 60 minutes, required 67 pounds of ozone per pound of TNT.	Sierka 1985
Hydrogen peroxide and ultraviolet light (Naval Weapons Support Center, Crane, Indiana; Army Medical Bioengineering Lab)	10 gal/min	Synthetic and actual pink water	Total organic carbon was reduced from 30-40 ppm to 5-8 ppm.	Andrews 1980 Moss and Chyrek 1984
Calcium hypochlorite [Ca(ClO) ₂] (University of Minnesota)	Pilot-scale plant	TNT from cleaning and dismantling of shells	Requires a 10-to-1 weight ratio of calcium hypochlorite to TNT. TNT destruction was essentially complete.	Semmens, Barnes, and O'Hara 1985

While ultrasound energy enhanced the ozonation of TNT, Sierka (1985) did not identify the role played by the sonic energy. Other species in the solution may preferentially absorb the ultrasound energy and reduce its effectiveness.

The organic species present in red water are primarily nitrosulfonates. Their oxidizability has not been tested. Red water also contains oxidizable inorganic salts (sodium nitrite and sodium sulfite), which may compete with organic matter for the oxidizing agents. Nitrites and sulfites will probably be oxidized to some extent, which would increase the quantity and cost of oxidizing agents required. This would also increase the equipment size required and the cost.

The fate of chemically combined nitrogen such as nitrates, nitrites, and organic nitro groups during chemical oxidation has not been established. Nitrogen oxide emissions could be significant.

No reaction parameters (e.g., pH, temperature, or reactor residence time) have been established for red water, even at the bench scale.

Scale-ups of technology that require the passage of a gas through a solution (ozonation) or the passage of ultraviolet and/or ultrasonic radiation through a solution will not be straightforward. Ozone and hydrogen peroxide may decompose in solution, especially if the solution has to be heated.

In summary, the technology has not been tested on any of the principal red water constituents, oxidation products may be even more toxic than the original red water constituents, and any precipitate formed by oxidation would have an impact on the transmission of ultraviolet light and ultrasound energy.

Current Application and Status of Technology

All work to date has been aimed at the development of methods for treating pink water. In the TNT production process, pink water is generated by water washing partially purified TNT after sellite (sodium sulfite) treatment. Wastewater for loading, assembling, and packaging TNT and RDX has also been called pink water. Pink water is an aqueous solution of TNT and related compounds (RDX, HMX, and WAX) with TNT concentrations of about 30 mg/L and total solids, including sodium sulfates and nitrates, of about 2 g/L.

Liquid-phase oxidations have been evaluated primarily on a bench scale, although Andrews (1980) tested hydrogen peroxide oxidation combined with ultraviolet light on a 10-gal/min scale.* On a 24-hour/day basis, this would be 14,400 gal/day. This scale would be sufficient to treat the red water produced at Radford in a 100-ton/day plant. Although these processes were intended to treat pink water, none was adopted for production-scale processing. Scale-ups from bench- to full-scale operation requiring gas-liquid contact (ozonation) or the diffusion of ultraviolet light or ultrasound through a liquid phase (ozonation and hydrogen peroxide) may not be straightforward.

Environmental Impact

In treated wastewater solutions, 50 percent or more of the original total organic carbon is present in solution as unidentified organic compounds. This is unacceptable for a RCRA-classified hazardous waste. Neither RAAP red water nor a similar material has been tested to determine what, if any, air emissions would be generated from the oxidation reactions. Nor has the issue of controlling emissions of unreacted ozone or chlorine (from sodium hypochlorite) from a scaled-up facility been addressed. With regard to solid/hazardous waste regulations, the discharge of unidentified organic compounds resulting from the treatment of a RCRA hazardous waste is unacceptable. None of the waste streams would be recyclable.

Time and Cost for Implementation

The technology is probably economically unacceptable because of the cost of chemical oxidizing agents. Calcium hypochlorite costs 9.35 cents per pound (Chemical Marketing Reporter 1989). At a 10-to-1 weight ratio of calcium hypochlorite to TNT (Simmens, Barnes, and O'Hara 1985), the chemical cost is 93.5 cents per pound. Treating the 0.64 pound of organic matter in a gallon of red water would cost 60 cents.

No values were presented for hydrogen peroxide consumption, but the material costs 64 cents per pound (Chemical Marketing Reporter 1989) and contains 47 percent active oxygen (O/H_2O_2 or 16/34). Thus, 265 g of active

* Personal communication from C. C. Andrews, Weapons Quality Engineering Center, Naval Weapons Support Center, Crane, Indiana, February 14, 1989.

oxygen would be required to convert the seven carbons and five hydrogens in sodium dinitrotoluene sulfonate (molecular weight, 284) to carbon dioxide and water. At 100 percent efficiency (unlikely), the hydrogen peroxide cost would be \$1.27 per pound of organic or 81 cents per gallon of red water.

Ozone is always generated on site by passing pure oxygen through an electric discharge. In a commercial-scale reactor, ozone is estimated to cost \$562 per pound.* At 67 pounds of ozone per pound of TNT (Sierka 1985), this cost would be prohibitive. The potential exists to reduce the chemical oxygen demand exerted by the sulfite by preoxidation with a less costly oxidant. Satisfying the COD generated by the sulfite would then reduce the volume of ozone required, and thus appear to make the overall process more economically favorable.

Performing preoxidation would require additional hardware (equipment) and process controls for the additional step in the treatment train, which could offset the savings realized by reduced ozone requirements. The technology is too poorly defined to attempt to estimate capital costs.

These costs may be compared with the cost of fuel for incineration. If 10,000 Btu is required to incinerate a gallon of red water and fuel costs \$3 per million Btu, the fuel cost for incineration would be 3 cents per gallon.

This technology should not be pursued for red water treatment. It could be considered for polishing a dilute stream of contaminated water from another treatment process if the difficulties of disposing of residues from treating a RCRA hazardous waste could be surmounted.

Complexity, Operation, and Flexibility

No actual process exists unless the influent and effluent are defined, and the effluent must comply with applicable regulations for the treatment of a hazardous waste.

Evaluation Summary

Table D-4 presents a quantitative evaluation of the liquid-phase oxidation process based on five categories of evaluation criteria. The final score for liquid-phase oxidation is 53 of a possible 110 points.

* Personal communication from J. Zarzycki, PCI Ozone Corporation, West Caldwell, New Jersey, May 16, 1989.

TABLE D-4. QUANTITATIVE EVALUATION OF LIQUID-PHASE OXIDATION

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	6
2. Current application and status of technology	7
3. Environmental impact	27
Wastewater discharge regulations	3
Air emission regulations	7
Solid/hazardous waste regulations	17
Recyclability	0
4. Time and cost for implementation	4
Time	2
Cost	2
5. Complexity, operation, and flexibility	9
Process complexity	2
Difficulty of operation	3
Flexibility of operating parameters	3
Miscellaneous	1
TOTAL	53

SOLIDS PRECIPITATION WITH SURFACTANTS

TECHNOLOGY DESCRIPTION

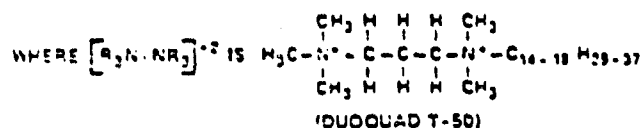
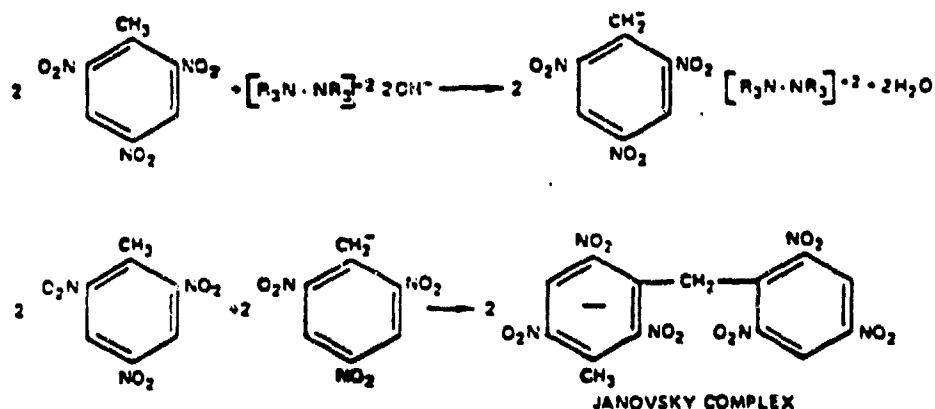
The surfactant technology has been investigated as a method of treating wastewater from TNT and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) loading, assembling, and packing (pink water). Because red water and pink water contain similar organic components, the surfactant technology has also been considered as a treatment for red water.

Scientists at the U.S. Army Armament Research and Development Command (AARADCOM), Dover, New Jersey, carried out 2-L laboratory-scale investigations of precipitating TNT, other explosives, and related compounds from a dilute solution (100 mg/liter typical) with the use of commercial surfactants (Freeman 1984). The reactive groups in the surfactant molecules were amino and quaternary ammonium groups. Additional work at Brooklyn Polytechnic Institute, Brooklyn, New York, was supported by AARADCOM (Okamoto et al. 1982). Both synthetic solutions and pink water from the Louisiana Army Ammunition Plant were used in the investigations.

Essentially complete precipitation was obtained of organic molecules having a methyl group and at least two nitro groups ortho and/or para to the methyl group on the benzene ring. (Trinitrobenzene, although lacking a methyl group, also precipitated.) Removal efficiency depended on:

- ° Choice of surfactant
- ° Reaction temperature (range investigated was 25° to 55°C)
- ° pH (range investigated was 11 to 12)
- ° Reactor residence time (range investigated was 18 minutes to 24 hours)

The proposed reactions for TNT precipitation with surfactants are as follows (Freeman 1984):



Note: One mole of surfactant reacts with and precipitates four moles of TNT.

Preliminary experiments with red water were carried out at Brooklyn Polytechnic Institute, but the work was not continued long enough to determine the applicability of surfactant technology to red water (Okamoto et al. 1982). The following problems were encountered*:

- ° A clear effluent was not obtained.
- ° An excessive amount of surfactant was needed for precipitation, and the surfactant is toxic.
- ° Incineration appears to be the most feasible method of disposing of the precipitate. Questions as to what would remain of the precipitate and what would be evolved upon incineration were unresolved.

Table D-5 lists the organic compounds found in RAAP red water. Although nothing has been published to indicate that surfactant precipitation of any red water constituent making up 0.5 percent or more of the red water solids has been attempted, most of the principal organic constituents of RAAP red water have a methyl group and two or more nitro groups ortho and/or para to

* Personal communication from J. Carrazza, U.S. Army R&D Command, Dover, New Jersey, February 15, 1989.

TABLE D-5. POTENTIAL REACTIVITY OF NITROBODIES FOUND IN
RAAP RED WATER TREATED WITH SURFACTANTS

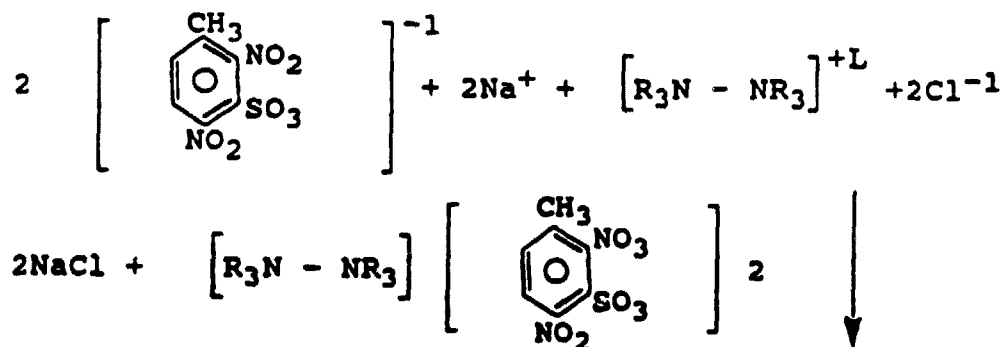
Nitrobody	Wt. percent in red water solids	Has a methyl group and two or more nitro groups ortho or para	Tested with surfactant	Precipitated with surfactant
Sodium sulfonate of 2,4,5-TNT	22.7	Yes	No	No
Alpha-TNT-sellite complex	16.2	Yes	No	No
Sodium sulfonate of 2,3,4-TNT	9.6	Yes	No	No
Sodium sulfonate of 2,3,6-TNT	2.0	Yes	No	No
Sodium sulfonate of 2,4,5-TNT	Trace	Yes	No	No
2,4,6-Trinitrobenzoic acid, sodium salt	1.0	No	No	No
Trinitrobenzaldehyde	1.0	Yes	No	No
Trinitrobenzyl alcohol	1.0	Yes	No	No
White compound, sodium salt	1.0	Unknown ^a	No	No
Sodium nitroformate	0.5	No	No	No
3,4-Dinitrobenzoic acid, sodium salt	Trace	No	No	No
2,3-Dinitrobenzoic acid, sodium salt	Trace	No	No	No
Trinitrobenzene sellite complex	Trace	No	No	No
2,4-Dinitrotoluene	Trace	No	Yes	93% complete
Alpha TNT	Trace	Yes	Yes	Complete

^a The identity of this compound is unknown (personal communication from J. Carrazza, U.S. Army, R&D Command, Dover, New Jersey, May 5, 1988).

the methyl group and could be precipitated by use of the surfactant technology. The definition of a methyl group has been broadened to include having at least one hydrogen attached to a nonring carbon. Thus, the nitrobenzaldehydes and nitrobenzyl alcohol are included, but nitrobenzoic acids are not. It should also be noted, however, that surfactants precipitated trinitrobenzene, which does not have a methyl group.

Differences between red water and pink water are as follows:

- ° Red water has about 15 percent dissolved solids, and about 55 percent of these solids are potentially precipitable with a surfactant. Because a precipitated solid may contain from 10 to 90 percent water, the solids precipitated from red water could entrain significant amounts of the total liquid fed to a reactor.
- ° Most of the red water solids are ionic compounds, whereas pink water solids are primarily covalent organic compounds. Red water solids include sodium nitrate, nitrite, sulfate, sulfite, and sodium salts of organic acids. These will also be entrained in the precipitate; and if the precipitate is incinerated, the ash generated will require disposal. Most of this ash will be water-soluble and therefore leachable. Material precipitated from pink water would have far fewer solids remaining after incineration.
- ° The proposed reaction mechanism for extracting a hydrogen from a methyl group will be much more difficult from a negatively charged ion than from a neutral molecule. For example, the ionization constant of the second hydrogen of a dibasic organic acid is usually about 0.001 that of the first hydrogen (oxalic acid is an example).
- ° In the second-stage reaction with pink water, the ionic compound formed between the surfactant and TNT reacts with two neutral TNT molecules to form a precipitate with one mole of surfactant and four moles of TNT. Almost all of the nitrobenzenes in red water are ionic species. The compositions and solubilities of reaction products have not been established. One possible reaction would be as follows:



In this reaction, one mole of surfactant would precipitate two, not four, moles of nitro bodies. This reaction involves the combination of an anion and a cation rather than molecular condensation at the methyl group. The preliminary investigations of applying surfactant technology to red water failed to produce a clear effluent. The chemistry has not been established and may differ from that of pink water.

Assuming that one mole of surfactant can quantitatively precipitate two moles of nitro bodies, other problems remain. The preferred surfactant in the pink water work was Duoquad T-50. According to the manufacturer, AKZO Chemical Company, the composition ranges between $C_{22}H_{25}Cl_2$ with a molecular weight of 413 and $C_{26}H_{58}Cl_2$ with a molecular weight of 469.* Based on an average molecular weight of 441 (the mean of 413 and 469) and the assumption that all nitro bodies have a molecular weight of 284 (the molecular weight of sodium dinitrotoluene sulfonate), 441 pounds of surfactant reacts with 568 (284×2) pounds of nitro bodies, or 0.78 pound of surfactant reacts with 1 pound of nitro bodies. With an allowance for a 10 percent excess of surfactant, 0.86 pound of surfactant would be required per pound of nitro bodies. The RAAP red water analysis indicates that a gallon of red water contains 0.76 pound of nitro bodies, which would require 0.65 pound of surfactant. AKZO Chemical quoted \$1.16 per pound for drums of surfactant in truckload lots or \$1.06 per pound in bulk.* Thus, the cost of surfactant per gallon of red water treated would be \$0.69 (see Eq. 1).

$$\frac{0.76 \text{ lb nitro bodies}}{\text{gal red water}} \times \frac{0.86 \text{ lb surfactant}}{\text{lb nitro bodies}} \times \frac{\$1.06}{\text{lb surfactant}} = \$0.69/\text{gal red water} \quad (\text{Eq. 1})$$

A gallon of the effluent from the precipitation step would contain 0.62 pound of inorganic solids originally present in the red water ($NaNO_3$, $NaNO_2$, $NaSO_4$, Na_2SO_3), 0.16 pound of sodium chloride formed by the precipitation reaction, and 0.06 pound of excess surfactant, for a total of 0.84 pound per gallon of dissolved solids. The surfactant, which has been used as a biocide, is toxic; therefore, the effluent could not be discharged without treatment.

A dry-appearing filtered precipitate will contain appreciable water. Assuming that the filtered precipitate entrains 1 pound of the supernatant

* Personal communication from J. Sinderwald, AKZO Chemical Co., Chicago, Illinois, May 1, 1989.

liquid per pound of precipitate (filtered and air-dried sludge from a municipal waste treatment plant is typically 90 percent or more water), a pound of precipitate will entrain 0.09 pound of inorganic salts, 0.007 pound of surfactant, and 0.9 pound of water. Therefore, the 1.35 pounds of precipitate formed from the treatment of 1 gallon of red water would entrain 1.2 pounds of water, or about 15 percent of all of the water present in the red water being treated. Only 85 percent of the water present in red water would become part of the effluent. If the precipitate entrained more than 1 pound of solution per pound of precipitate, which is quite possible, more than 15 percent of the solution being treated would become part of the precipitate. In any event, both the precipitate and the supernatant liquid would require further treatment.

The precipitate probably could not be landfilled. In work published by the U.S. Army Natick R&D Laboratories, Natick, Massachusetts (Kaplan and Kaplan 1982), the precipitates formed from surfactant treatment of pink water were determined to be mutagenic and leachable from soil. Therefore, incineration is probably the most acceptable means of disposal. The inorganic salts would remain as water-soluble (and leachable) oxides and sulfates, which would require further treatment.

Because it uses a toxic solution, expends an expensive reagent, produces an effluent that is toxic, and produces a precipitate that requires incineration, the surfactant technology has neither technical nor economic advantages over direct red water incineration.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The theoretical potential for precipitation of red water solids with surfactants is relatively high. In laboratory investigations of both synthetic solutions and pink water, essentially complete precipitation was obtained of organic molecules having a methyl group and at least two nitro groups ortho and/or para to the methyl group. This configuration is characteristic of the principal nitrocompounds present in red water.

Current Application and Status of Technology

The surfactant technology has been investigated at the bench scale for the treatment of pink water; however, preliminary experiments with red water failed to produce a clear effluent. The reaction mechanism for red water has not been established and may differ from that of pink water. Furthermore, the solubilities of the reaction products between surfactant cations and red water anions are unknown.

Environmental Impact

Wastewater Discharge Regulations--

The effluent from precipitation of red water solids with a surfactant will contain excess surfactant, which is toxic. A method for treating or disposing of this stream has not been addressed.

Air Emission Regulations--

Precipitation of red water solids should not produce air emissions; however, disposal of the precipitate may. No testing has been conducted to determine what, if any, emission controls will be required.

Solid/Hazardous Waste Regulations--

Solids precipitated by this technology will be classified as a hazardous waste. Although the solids may be incinerated, no method of handling the resultant ash has been addressed. Similarly, no method of treating the effluent, which will also be hazardous, has been addressed.

Recyclability--

None of the waste streams from precipitation of red water solids are expected to be recyclable.

Capital and O&M Costs

No capital costs have been estimated because methods for treating the precipitate and effluent have not been defined. Operating costs for the surfactant alone are estimated to be \$0.69 per gallon of red water (or \$690 per 1000 gallons), which is prohibitively expensive.

Complexity, Operation, and Flexibility

Because the treatment train for this process has not been defined, process complexity, difficulty of operation, and flexibility of operating parameters are difficult to evaluate. Precipitation and filtration can be readily scaled up from bench-scale investigations.

Evaluation Summary

Table D-6 presents a quantitative evaluation of the surfactant technology based on five categories of evaluation criteria. The final score for precipitation of red water solids with a surfactant is 27 of a possible 110 points.

TABLE D-6. QUANTITATIVE EVALUATION OF SOLIDS PRECIPITATION WITH A SURFACTANT

		<u>Points awarded</u>
1.	Theoretical potential for red water treatment	7
2.	Current application and status of technology	7
3.	Environmental impact	6
	Wastewater discharge regulations	0
	Air emission regulations	6
	Solid/hazardous waste regulations	0
	Recyclability	0
4.	Time and cost for implementation	4
	Time	2
	Cost	2
5.	Complexity, operation, and flexibility	3
	Process complexity	1
	Difficulty of operation	1
	Flexibility of operating parameters	1
	Miscellaneous	0
TOTAL		27

WET AIR OXIDATION

TECHNOLOGY DESCRIPTION

Wet air oxidation (WAO) is the oxidation of material in aqueous solution or suspension in the presence of air at a temperature above the normal boiling point of water. The higher temperature increases reaction rates and allows the air oxidation of matter that would not normally be oxidizable. The atmospheric pressure is also increased to maintain water in the liquid phase and to increase the solubility of air (oxygen) in water. Typical reaction conditions are temperatures between 175° and 327°C (347° to 621°F) and pressures between 2,096 and 20,690 kilopascals (300 to 3000 psig) (Zimpro/Passavant Corporation, undated).

The reactor is a pressure vessel that would probably be made of 304 or 316 stainless steel if used for red water oxidation. Auxiliary equipment would include a high-pressure pump (to bring red water into the reactor), an air compressor (to provide high-pressure air), a separator (to separate gases from oxidized red water), and heat exchangers. Possible conditions for red water oxidation would be 1300 psi at 300°C (572°F), a reactor residence time of 1 hour, and oxygen requirements of 0.9 pound per gallon of red water (50 percent excess). These conditions were used for a previous red water experimental program conducted by Zimpro in 1956 (Seidman 1956). Figure D-2 presents a general flow schematic for WAO.

In the WAO process, sodium sulfite is converted to sodium sulfate, sodium nitrite is converted to sodium nitrate, and sodium dinitrotoluene sulfonates are converted to carbon dioxide, water, and sodium sulfate plus nitrogen, nitrogen oxides, or sodium nitrate.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Based on laboratory studies conducted in 1956 on red water from Army ammunition plants, treatment of red water by wet air oxidation appears to be feasible.

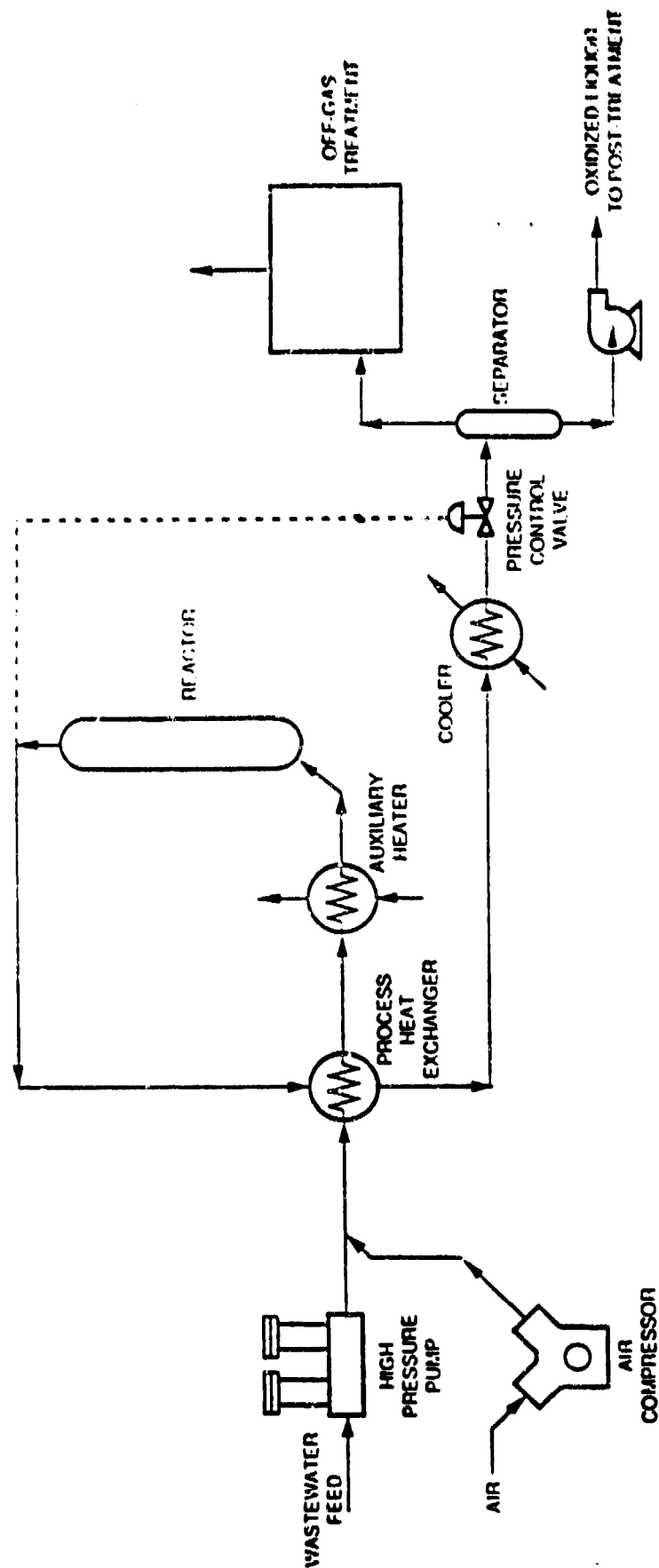


Figure D-2. Wet air oxidation general flow schematic.

Wet air oxidation has been successfully used on toxic wastes to achieve better than 95 percent oxidation of organic matter and to produce a residue that can be handled in a conventional wastewater treatment facility.

Because oxidation efficiency usually ranges between 95 and 100 percent, subsequent treatment of the aqueous stream from the reactor will be required (Seidman 1956). The effluent stream from a WAO reactor is probably eligible for delisting as a hazardous waste inasmuch as TNT processing wastes (K047) are so classified because of reactivity rather than the presence of any specific chemical compound.

Wet air oxidation has been used successfully to treat other toxic wastes, such as cyanide plating wastes. The technology has been scaled up successfully for other applications based on laboratory-scale investigations similar to those conducted with red water.

Current Application and Status of Technology

More than 30 years ago, Zimpro Corporation (now Zimpro/Passavant Corporation) carried out laboratory-scale (150 to 325 mL) investigations of red water oxidation with red water obtained from the Joliet Arsenal-Kankakee facility in Elwood, Illinois, and the Volunteer Ordnance Works in Tyner, Tennessee (Seidman 1956). The chemical oxygen demand (COD) of the Joliet red water was reduced 97.1 percent from 65.2 to 0.9 g/L. Sodium sulfate and sodium nitrate accounted for 97 percent of the total solids present in the resulting material. The COD of the Volunteer red water was reduced 96 percent from 15.6 to 0.63 g/L. In both cases, the oxidized liquid was yellow and contained no undissolved solids except ferric oxide, which settled out at pH 6.9, as would be expected. Reaction conditions included 1 hour of oxidation at 300°C (572°F). The remaining oxidizable material (residual COD) in the oxidized red water was not identified.

Environmental Impact

Wastewater Discharge Regulations--

The TNT production wastes, such as those in red water, are classified as hazardous because of their reactivity rather than the presence of specific contaminants. For the WAO technology to be considered a viable option, the

wastewater must be delisted or certified to be no longer reactive. The following steps are required to initiate the delisting process*:

- ° Identify contents within system.
- ° Establish that the wastewater is no longer reactive.
- ° Establish the absence of all 40 CFR 261 Appendix VIII constituents.

The EPA subsequently reviews this information and decides whether the request is warranted. If it is, a notice is published in the Federal Register, and public comment is received and reviewed. The EPA makes a final determination within an estimated 12 to 18 months. Lake City Army Ammunition Plant has applied for delisting of its process wastewater.

Air Emissions Regulations--

Laboratory-scale studies did not indicate the presence of air emissions. Sulfites are oxidized to sulfates, and nitrites are oxidized to nitrates, which reduces the potential for sulfur dioxide and nitrogen oxide emissions.

Solid/Hazardous Waste Regulations--

The only solid/hazardous waste that may be generated in the treatment of red water by WAO is trivalent chromium, which may result from the attack of stainless steel processing equipment by nitric acid and sulfuric acid during the production process. Chromium and iron both precipitate out as trivalent hydrated oxides.

Because trivalent chromium oxide is water-insoluble, it will pass the EP toxicity test. Conversion of chromium to the trivalent state, followed by precipitation of the hydrated oxide, is the accepted technology for treating chromium-bearing wastes.

Recyclability--

The only materials with the possibility of reuse are sulfites. They are not recoverable, however, because they are oxidized to sulfates during the process.

Wet air oxidation would allow oxidation with air rather than expensive chemicals (e.g., hydrogen peroxide, ozone) and would not require the high fuel costs associated with thermal incineration.

* Personal communication from T. Grist, U.S. Environmental Protection Agency, Washington, D.C., May 16, 1989.

Development work would be required for the following:

- ° To determine the optimum pressure, temperature, and residence time. The cost of pressure vessels is related to the operating pressure. The pressure of superheated water is temperature-dependent.
- ° To determine required treatment procedures for the process effluent. It would be desirable for the effluent to be treatable in the existing plant wastewater treatment system.
- ° To determine suitable materials of construction for the pressure vessel and auxiliary equipment.

The major variables governing the WAO reaction are temperature, pressure, residence time, and percent oxygen in the injected gas. A small pilot-scale plant could be built to quantify the effect of these variables on effluent quality.

Time and Cost for Implementation

Rough estimates of the installed capital cost of a 15 gal/min (21,608 gal/day) unit with all required auxiliaries and operating at 300°C and 1300 psi range from \$2.0 to \$2.5 million.* Based on a capital cost of \$2.5 million for continuous operation and published cost guidelines (Perry and Green 1984; Peters and Timmerhaus 1980), estimated annual costs are as follows:

Capital recovery (10 yr, 10%)	\$407,000
Maintenance (10%)	250,000
Fuel for reactor, \$4/mm Btu	101,000
Electricity (263 hp), \$0.06/kWh	103,000
Operating labor (2 employees at \$20/h)	83,000
Supervision (25% of operating labor)	21,000
Insurance (1%)	<u>25,000</u>
TOTAL	\$990,000 or \$0.16/gal

The estimated annual costs of \$990,000 is conservative, as it is based on 365 days operation per year. An actual plant would operate a maximum of 300 days per year because of outages and scheduled maintenance shutdowns.

This evaluation assumes that the effluent is treatable in the plant wastewater treatment system and assigns no costs for this treatment.

* Personal communication from T. Randall, Zimpro/Passavant Corporation, Rothschild, Wisconsin, June 12, 1989.

Testing with RAAP red water would be particularly beneficial for optimizing process operating parameters and equipment selection for wet air oxidation, as small changes in temperature have a significant impact on the pressure of steam above the superheated water. For example:

Pressure = 1200 psi at 297°C (519°F)
 = 1300 psi at 303°C (577°F)
 = 1400 psi at 308°C (587°F)
 = 1500 psi at 313°C (596°F)

A rule of thumb is that each 10°C increase in temperature doubles the reaction rate. Consequently, as the pressure increases, the required residence time should decrease with an associated decrease in reactor size.

The reactor is a pressure vessel; a compressor supplies air for oxidation, and a pressure pump supplies red water for the reaction. Thus, the capital and operating costs for the equipment are sensitive to pressure. Experiments must be conducted to determine the most economical reactor size and corresponding operating conditions.

Complexity, Operation, and Flexibility

Process Complexity and Difficulty of Operation--

Oxidation takes place in a single stage in a single vessel; however, the reaction takes place in superheated water at high pressures. The process can be automated, and pressure relief valves can be used to ensure safe operation.

Flexibility of Operating Parameters--

The oxidation reaction rate and extent will probably be temperature-dependent. The temperature must be high enough to achieve a fast reaction rate and nearly complete oxidation. The pressure exerted by superheated water increases sharply with temperature. The reactor, pumps, and compressor must be properly designed to withstand the expected temperatures and pressures. Good process control will be essential. Conducting a full-scale operation appears to be plausible. Laboratory-scale investigations have been carried out with red water from other Army ammunition plants. Similar laboratory testing programs have been successfully used for other waste treatment scale-ups.

Miscellaneous--

The primary unpredictable variable is the requirement that the effluent be both delistable as a hazardous waste and also amenable to treatment in the plant wastewater treatment system.

Evaluation Summary

Table D-7 presents a quantitative evaluation of wet air oxidation based on five categories of evaluation criteria. The final score for the wet air oxidation process is 73 of a possible 110 points.

TABLE D-7. QUANTITATIVE EVALUATION OF WET AIR OXIDATION

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	9
2. Current application and status of technology	14
3. Environmental impact	30
Wastewater discharge regulations	5
Air emission regulations	9
Solid/hazardous waste regulations	16
Recyclability	0
4. Time and cost for implementation	7
Time	4
Cost	3
5. Complexity, operation, and flexibility	13
Process complexity	2
Difficulty of operation	3
Flexibility of operating parameters	3
Miscellaneous	5
TOTAL	73

HYBRID THERMAL TREATMENT SYSTEM (HTTS)

TECHNOLOGY DESCRIPTION

The Hybrid Thermal Treatment System (HTTS), developed by International Technology Corporation (IT), consists of a rotary kiln, a secondary combustion chamber (SCC) with a water quench chamber, a particulate scrubber system, and other support modules (Foster Wheeler 1988). Both the kiln and secondary combustion chamber burners can fire fuel oil, natural gas, and/or waste liquids (International Technology Corporation, undated). Figure D-3 presents a flow diagram of the HTTS system.

Rotary Kiln Incineration

The HTTS rotary kiln operates under semireduced conditions in a closely controlled air supply mode (International Technology Corporation, undated, and personal communication from R. Novak, International Technology Corporation, 1989). Because it operates under a much more controlled air environment (no excess air) than does a conventional rotary kiln, generation of NO_x is minimized. The kiln's main function is to evaporate water and to provide combustion of organics. It is primarily an evaporation system; much of the combustion takes place in the secondary combustion chamber. According to Mr. Novak, organics that are not oxidized in the kiln will be oxidized in the SCC.

Liquid and Gas Combustion

Gases generated in the kiln are incinerated in a vertical SCC designed to handle large variations in gas composition and volumes and to avoid entrainment of fine solids in the kiln gas. The SCC can operate continuously at 1200°C (International Technology Corporation, undated). The limiting factor of this secondary combustion process is the volume of gas the air pollution control system can handle, i.e., 75,000 cubic feet per minute.*

* Personal communication from C. Shell, International Technology Corporation, Knoxville, Tennessee, 1989.

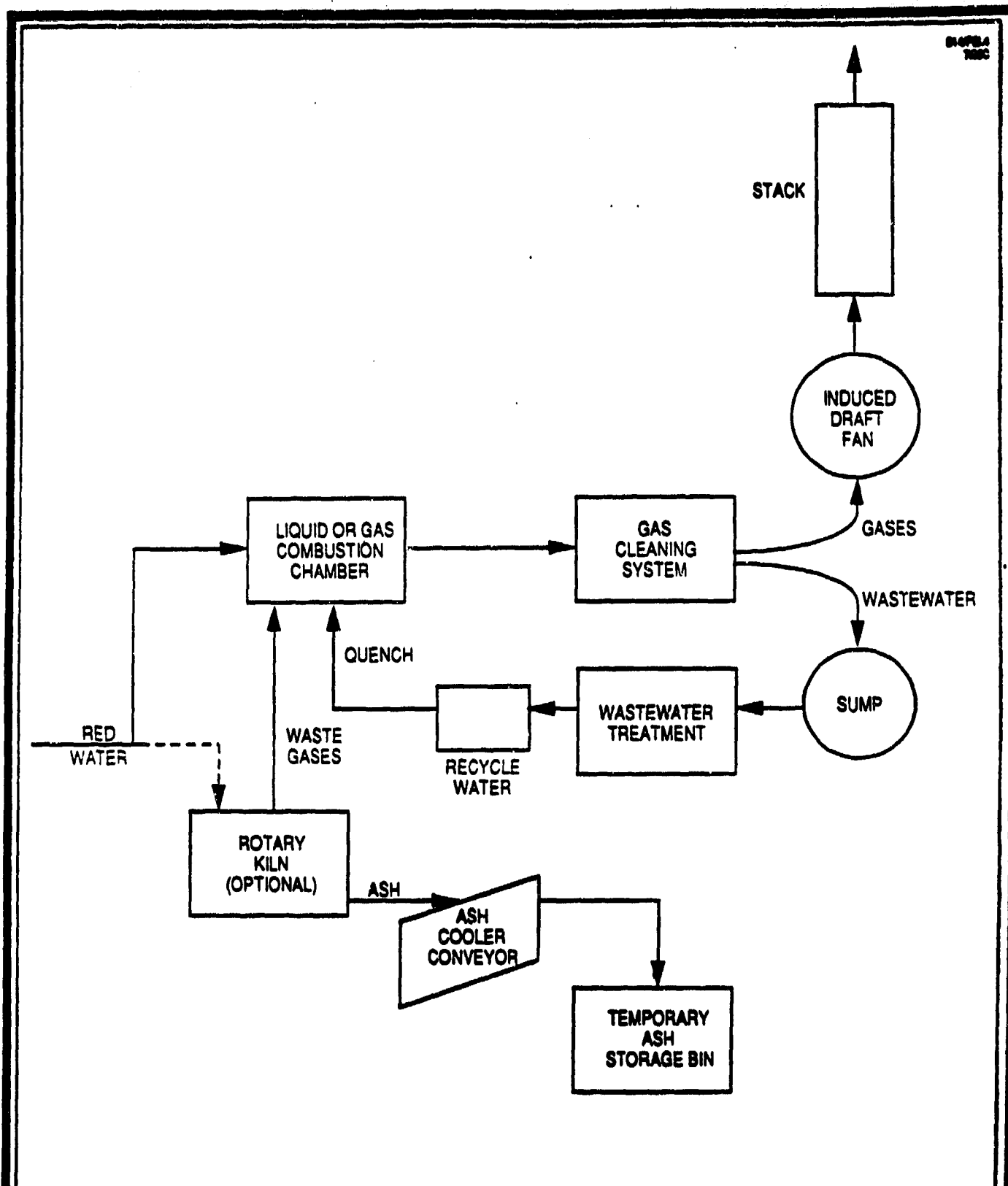


Figure D-3
PROCESS SCHEMATIC FOR TREATMENT OF
RED WATER USING THE HYBRID THERMAL
TREATMENT SYSTEM (HTTS)

SOURCE: IT, 1992.

HUNTER/ESE

Secondary Evaluation of
Red Water Treatment Technologies

For red water treatment, a three-zone liquid/gas combustion process has been proposed for use as the secondary combustion chamber after rotary kiln incineration. In the three-zone process, Zone 1 would provide an oxidizing environment to destroy aqueous organic wastes. Vapors and gases would be oxidized by the addition of excess oxygen, and maximum NO_x would be emitted. Zone 2 would provide a reducing environment (through the addition of a reducing agent such as methane gas) to destroy NO_x . Zone 3 would provide a low oxidizing environment to destroy combustible fumes (including H_2 and CO).^{*} Because the secondary combustion chamber will directly oxidize aqueous organic wastes, the initial rotary kiln process may not be necessary.

Water and Air Pollution Control

The SCC gases are quenched with water and then processed through an air pollution control module capable of removing submicrometer particulate matter and acid gases. Treated gases are then pulled through a stack by an induced-draft fan. After their separation from the scrubber water, solids can be added to the kiln ashes. The scrubber water is then tested and recycled, which minimizes water consumption. The wastewater effluent can be readily treated prior to discharge (International Technology Corporation, undated).

Demonstrated Waste Treatment

The HTTS has been used at the Cornhusker Army Ammunition Plant (CAAP) to treat soils contaminated by the leaching of TNT- and RDX-contaminated wastes. The HTTS successfully processed the contaminated soil, and discharges met applicable regulations (Foster Wheeler 1988). During the use of the HTTS at CAAP, the vertical SCC was operated at 1000°C . Downstream of the water quench section the temperature was 80°C (Foster Wheeler 1988).

No information has been obtained regarding the use of the HTTS with liquid wastes. Pretreatment may be required to concentrate red water prior to incineration. Fuel requirements for the combustion of red water may be high because of the high water content of the waste. Waste streams generated during HTTS red water treatment that may require further treatment include incinerator ash and blowdown water. Incinerator ash will consist primarily of water-soluble sodium sulfate. Metals, which are concentrated in this and

^{*} Personal communication from R. Novak, International Technology Corporation, 1989.

other incineration processes, may pose a problem in the ash. Unoxidized organics also may be present in the ash. Blowdown water, which contains Na_2SO_3 , Na_2SO_4 , and Na_2CO_3 , must be disposed of (Foster Wheeler 1988).

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The HTTS technology has not been tested on red water. The theoretical potential of HTTS for effective treatment of red water is relatively low because it has been tested only on soils (not aqueous wastes). International Technology Corporation maintains that the system can be used to treat aqueous wastes by pumping liquid wastes to the thermal treatment devices under monitored and controlled conditions. Identification and maintenance of these conditions may be difficult (DeCicco and Troxler, undated).

Significant data gaps and problem areas exist for evaluation of the potential for effective red water treatment with HTTS. These data gaps are as follows:

- 1) Because the treatment of liquid wastes with HTTS has not been demonstrated, the technical feasibility of this technology for red water treatment is uncertain.
- 2) The two oxidation steps in the proposed liquid/gas combustion process are proven processes; however, the reduction step (for reduction of NO_x) is not well demonstrated.
- 3) The presence of alkali metal salts may cause operational problems that lead to formation of submicrometer particulates, formation of low-melting slag eutectics, and metal corrosion. Crystals of sodium sulfate remaining after combustion may adhere to the hearth and make cleaning difficult.*
- 4) Because the ash is water-soluble, leachability problems are expected if the untreated ash is landfilled.*
- 5) If the liquid/gas combustion chamber is used alone (not following rotary kiln incineration), the waste must be atomized through an atomization nozzle with steam or high-pressure air, which can result in high amounts of suspended particulates.* Also, solids such as sodium salts may build up in the liquid combustor.**
- 6) The presence of heavy metals may be associated with residues from the gas-cleaning system and may prevent delisting of ash (DeCicco and Troxler, undated).

* Personal communication from R. Novak, International Technology Corporation, 1989.

** Personal communication from C. Fumer, International Technology Corporation, 1989.

- 7) Scale-up capabilities are uncertain for use of the HTTS in treating liquid wastes because the technology has only been used at full-scale to treat solid wastes.

Current Application and Status of Technology

The HTTS process has been demonstrated on a full-scale basis by the treatment of 22,000 tons of explosives-contaminated soil at CAAP. The TNT and RDX removal efficiencies were 99.99 percent. A three-stage process for effective red water treatment has been designed that will meet air emission standards by removing 99.9 percent of NO_x emissions.

Environmental Impact

Based on theoretical evaluations, air emissions should be reduced to acceptable levels through the proposed reduction step. International Technology Corporation maintains that the ash resulting from HTTS, which consists primarily of water-soluble sodium sulfate, may be of higher quality and less variable than that of conventional rotary kiln incineration; however, this has not been demonstrated. Also, process water purged from the quench system can be treated in a wastewater treatment system to neutralize acids and remove heavy metals.*

Time and Cost for Implementation, Capital and O&M Costs

Implementation to full scale is more difficult for liquid treatment, since only full-scale treatment of soils has been implemented in the past. In order for the HTTS to be implemented at a full-scale level for red water treatment, laboratory testing and design modifications must take place. IT Corporation has estimated that the time required for this preliminary testing and design will range from 6 to 9 months. The cost associated with this has been estimated at \$100,000 to \$300,000. These estimates of implementation time and costs do not include construction of the full-scale system.

Based on an assumed treatment of 16,250 gallons of red water per day, the capital cost for an HTTS consisting of a rotary kiln and a three-stage

* Personal communications from R. Novak, International Technology Corporation, 1989.

secondary combustion chamber is approximately \$10 million. The O&M costs for such a system have been estimated at approximately \$1100/1000 gallons. These costs are based on the assumption that a dual-control, continuously monitored system will be used. The O&M costs are based on the assumption that the system will run 24 hours per day, 365 days a year. The estimate includes costs for electricity, fuel, health and safety, quality assurance/quality control (QA/QC), operations personnel, maintenance personnel, and supplies.*

The capital cost of the liquid/gas combustion chamber alone (without prior rotary kiln incineration) has been estimated at \$8 million. The O&M costs for this system will be approximately \$110/1000 gallons. These costs are based on the previously stated assumptions.**

Complexity, Operation, and Flexibility

The HTTS is relatively complex, particularly when it includes the secondary process proposed for red water treatment. Operation is also relatively difficult because of the extensive monitoring required for the system. Laboratory and pilot-scale testing with red water will probably be necessary to assure effective treatment. Operating parameters are not particularly flexible because these parameters, when established, must be closely maintained to provide adequate treatment of the red water. Implementation to full scale is more difficult for liquid treatment, as only full-scale treatment of soils has been implemented thus far.

Evaluation Summary

The overall evaluation of the process is not particularly favorable because the process has not been demonstrated for aqueous waste treatment. Significant modifications to the current HTTS technology may be required for use of this technology for red water treatment.

Table D-8 presents a quantitative evaluation of the technology based on five categories of evaluation criteria. The final score for the HTTS process is 57 of a possible 110 points.

* Personal communication from K. Smith, International Technology Corporation, 1989.

** Personal communication from K. Smith, International Technology Corporation, 1989.

TABLE D-8. QUANTITATIVE EVALUATION OF THE
HYBRID THERMAL TREATMENT SYSTEM (HTTS)

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	8
2. Current application and status of technology	16
3. Environmental Impact	17
Wastewater discharge regulations	5
Air emission regulations	5
Solid/hazardous waste regulations	7
Recyclability	0
4. Time and cost for implementation	8
Time	4
Cost	4
5. Complexity, operation, and flexibility	8
Process complexity	2
Difficulty of operation	2
Flexibility of operating parameters	2
Miscellaneous	2
TOTAL	57

PLASMA ARC

TECHNOLOGY DESCRIPTION

Background

Plasma arc is a thermal destruction process in which organic materials are converted to inorganic byproducts. The heat source is an electric arc that maintains a temperature of several thousand degrees centigrade, which converts a material to plasma when it is applied. Plasma, often called the fourth state of matter, is characterized by molecules separated even further than in gases. Inorganic byproducts of this process are formed upon recombination of atomic species. The process is typically performed in the absence of oxygen, which minimizes NO_x and SO_x production in nitrogen- and sulfur-rich materials.

Three manufacturers of plasma arc processes are identified in Foster Wheeler (1988): Westinghouse Environmental Services, Tetronics Research and Development Company, and SKF Plasma Technologies. The Westinghouse Environmental Services and Tetronics systems operate under the same general principle, i.e., materials are exposed directly to the electric arc. The SKF process differs in that a carrier gas is passed through a torch, where it picks up energy from the arc and then transfers the high-energy gas to the reaction zone in a furnace.

The Tetronics process was designed for application in the materials and metallurgical industries, and the SKF process was designed for the recovery of black liquor in the pulp and paper industry (Foster Wheeler 1988). Both of these processes are used in industry for these respective applications. Whether destruction of organic wastes by use of these processes has been evaluated is not known. Based on the available process descriptions, however, these processes do have potential for organic waste destruction. SKF has a pilot-scale unit available for performing tests with red water at its testing facility. Although Tetronics has a testing facility, a plasma test unit would have to be constructed to evaluate red water treatment.

The Westinghouse process is the only one of the three processes for which reference has been made to destruction of organic wastes (Foster Wheeler 1988). During one test burn with carbon tetrachloride, greater than 99.99 percent destruction was achieved. A second trial burn with PCBs resulted in a destruction efficiency of greater than 99.9999 percent. Westinghouse Environmental Services has a prototype unit that can be used for pilot tests.

Red water has not been treated by this process; however, Westinghouse Environmental Services did perform mass and energy balances for its prototype unit to determine red water byproducts (Foster Wheeler 1988). The red water was assumed to have the following composition, which is quite different from that provided in Appendix A:

<u>Component</u>	<u>Composition, wt. percent</u>
Sodium carbonate	5
Sodium sulfate	5
Sodium nitrite	4
TNT	7
Sulfonated TNT	12
Water	67
Total	100

The following recombination products would be expected:

<u>Component</u>	<u>Composition, wt. percent</u>
Water	66.4
Nitrogen	9.95
Hydrogen	8.66
Carbon dioxide	8.10
Carbon monoxide	2.41
Sodium sulfate	1.82
Sodium carbonate	0.618
Sulfur	0.472
Hydrogen sulfide	0.159
Sulfur dioxide	0.0757
Total	98.7

A scrubbing system will be necessary to remove the sulfur-containing compounds from the gas phase before it is released. Components formed upon atomic recombination and retained in the aqueous phase are amenable to conventional treatment processes.

Process Flow Description

Figure D-4 depicts the process flow diagram for the Westinghouse Environmental Services process. The process flow description is summarized as follows (Westinghouse Environmental Services 1988):

- 1) Waste is introduced to the process, and molecules are dissociated into their atomic components.
- 2) Atoms recombine in the reaction chamber to form gases, typically carbon monoxide, nitrogen, and hydrogen along with some lower-molecular-weight hydrocarbons (e.g., methane, ethane).
- 3) Acid gas is neutralized with caustic soda in a wet scrubber to form a salted water effluent. Particulate carbon produced is also removed from this stream.
- 4) The product gas is drawn off by an induction fan and flared directly.
- 5) When the waste feed is analyzed, the molecular components of the waste can be modeled by computer to give predicted gas values closely approximating those of the gas actually produced by the unit.

The unit is started by electrically powering the torch, which instantaneously creates the plasma. Operation begins with the use of a nontoxic solvent feed (e.g., methanol) and is continued for approximately 20 minutes until the reactor stabilizes at a predetermined temperature, typically around 1200°C. Stable reaction chamber temperatures indicate adequate quenching of the torch power, which ensures efficient destruction of the incoming waste. The destruction process is pyrolytic in nature. The reaction chamber temperature is controlled by adjusting torch power, waste feed flow, or torch process gas flow and is established to control the types of recombination products being formed. The entire system is controlled by process computer through a series of temperature, electrical, and flow sensors. While the operation of the unit is monitored and directed by a technically experienced person, the computer has overriding control. This is based on a series of control parameters set according to operational limits by which system efficiency can be ensured and risk to the environment can be eliminated.

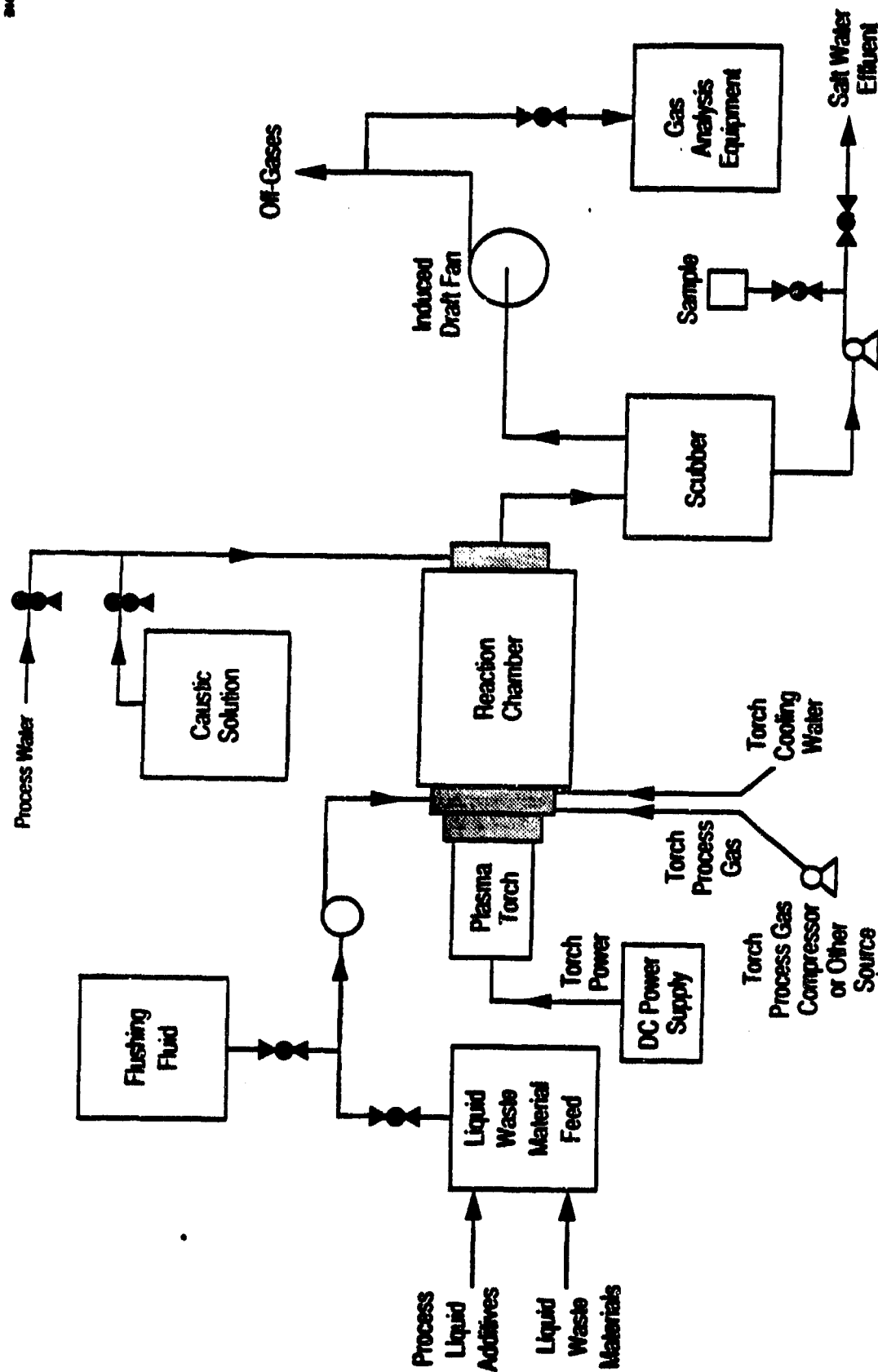


Figure D-4
WESTINGHOUSE - PYROPLASM SYSTEM

SOURCE: WESTINGHOUSE, 1981.

HUNTER/WESE

Secondary Evaluation of
Red Water Treatment Technologies

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Based on the process flow description presented in the preceding subsection, the plasma arc process has a high theoretical potential for treating red water. Although in theory the process seems suitable for destruction of organic wastes and is capable of evaporating water, it is not considered practical for use on wastes with high water content, such as red water.* Generally, the process is not recommended for treatment of wastes with a water content greater than 20 percent.

Current Application and Status of Technology

Red water has not been treated using this process; however, as discussed previously, mass and energy balances have been performed for treatment of red water in the plasma arc process. Because the application of the plasma arc process has been evaluated only in a paper study, its application for treatment of red water remains strictly conceptual. Based on historical data pertaining to PCB and carbon tetrachloride destruction by the process, however, red water destruction of 99.9999 percent is expected to be achieved (Foster Wheeler 1988).

Environmental Impact

Wastewater Discharge Regulations--

Acid gases generated by the process are quenched in the wet scrubber, which yields the only wastewater generated by the process. This wastewater can be discharged to a publicly owned treatment works. If effluent from the process must be discharged to a ground-water reinjection well or to surface water, however, additional treatment may be necessary to remove soluble salts.

Air Emission Regulations--

Acid gases formed in the process are quenched in a caustic soda solution before being discharged. After the wet scrubber, contaminants remaining in the gas formed in the reaction chamber (hydrocarbons such as methane and

* Personal communication from B. Reed, Westinghouse Environmental Services, 1989.

ethane) are flared off. The process is well equipped to manage air emissions; therefore, meeting air emission regulations is not expected to be difficult.

Solid/Hazardous Waste Regulations--

Carbon particulates represent the only solids produced in the process. The majority of carbon particulates will be collected in the wet scrubber, but some carbon will build up on the walls of the reactor and require periodic removal. The only liquid waste the process produces is scrubber water. Assuming these treatment residuals (scrubber water and carbon solids removed from the reactor) can be delisted, the materials formed in the process can be treated as nonhazardous.

Recyclability--

The process is totally destructive with respect to the liquid phase. The only possibility of recovering materials for reuse in TNT manufacturing entails collecting and cleaning the stack gases. Blending of waste prior to destruction can alter gas constituents and their relative amounts to the desired ranges. Which materials can be added to the process to allow recovery of materials for use in TNT manufacturing (e.g., NO_3) or whether recycling will be cost-effective is not currently known.

Time and Cost for Implementation

A mobile pilot-scale unit is available for testing the treatment of red water at a rate of 3 gal/min. Results can be used to assess the effectiveness of red water treatment and to define design parameters for the plasma arc process. Pilot tests could be completed in a period of 6 to 9 months. This includes time for development of a testing plan, system modification, and the actual testing. Costs for these tests are expected to be less than \$500,000. Design of a full-scale unit can proceed upon completion of the pilot tests. This would be expected to take 6 to 12 months and to cost less than \$500,000. Therefore, the estimated time to implementation of the treatment technology is approximately 12 to 21 months, and the estimated cost is approximately \$1,000,000 (not including procurement of equipment, construction, or installation of the designed treatment unit).

Based on operating 24 hours a day, the design capacity of the plasma arc process would be 11.3 gal/min or 16,250 gal/day. The largest unit in operation for the destruction of organic wastes has a capacity of 3 gal/min. Obviously, a larger unit would have to be designed for treatment of red water, but scale-up of the process is believed to be possible.* The capital cost of the 3-gal/min unit is approximately \$3 million. Based on the high water content of red water, the expected flow rate of a 3-gal/min unit would be lower (e.g., 1 to 2 gal/min) to achieve the desired destruction.

For the purposes of estimating capital costs for the treatment unit, a minimum of four 3-gal/min units would be required to treat the expected flow of red water. Although the process can be scaled up to treat the 11.3-gal/min design flow, no costs for such a unit are available at this time; therefore, the estimated capital costs for the process are approximately \$12 million.

Operation and maintenance costs involve electricity, labor, operation of the air pollution control devices, and other miscellaneous items. Some wastes with a lower water content than that of red water have cost as much as \$1/lb to treat. Costs for treatment of red water are expected to exceed \$9200/1000 gallons (\$1/lb) because of the high water content.

Complexity, Operation, and Flexibility

Process Complexity--

The plasma arc process is not considered complex; waste destruction is achieved early in the process, and the remainder of the process is devoted to treatment of newly formed gases. Waste enters at the torch, where it is atomized; it is then passed to the reaction chamber, where molecules combine. From the reaction chamber, gases are processed through a wet scrubber before being released.

Difficulty of Operation--

Two trained operators are on hand at all times during operation of the process, but the treatment system is automated.

* Personal communication from B. Reed, Westinghouse Environmental Services, 1989.

Flexibility of Operating Parameters--

The process has the flexibility to alter the gases generated. The feed stream is analyzed, and computer models are used to predict the gases that will be generated. Careful blending of the waste prior to its destruction can alter gas constituents and concentrations. The process also has the flexibility to achieve complete destruction of red water despite varying concentrations of organics in the waste.

Miscellaneous--

A prototype unit has been subjected to extensive testing and has proved that the technology is technically feasible for treatment of organic wastes. The process has also been demonstrated to be reliable in tests with the prototype unit. The principal disadvantage of this process is the cost of evaporating water while organics are being destroyed. Typically, the process is limited to wastes with a water content of less than 20 percent.

Evaluation Summary

Table D-9 presents a quantitative evaluation of the plasma arc process based on five categories of evaluation criteria. The final score for the plasma arc process is 64 of a possible 110 points.

TABLE D-9. QUANTITATIVE EVALUATION OF THE PLASMA ARC PROCESS

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	5
2. Current application and status of technology	11
3. Environmental impact	35
Wastewater discharge regulations	9
Air emissions regulations	9
Solid/hazardous waste regulations	17
Recyclability	0
4. Time and cost for implementation	5
Time	3
Cost	2
5. Complexity, operation, and flexibility	8
Process complexity	3
Difficulty of operation	2
Flexibility of parameters	2
Miscellaneous	1
TOTAL	64

SLAGGING ROTARY KILN

TECHNOLOGY DESCRIPTION

Background

Incineration by slagging rotary kiln (SRK) is a process in which wastes are incinerated in a rotary kiln at a temperature higher than that of a standard rotary kiln, which results in the generation of slag and combustion gases. Temperatures in the rotary incinerator of an SRK generally range from 1100° to 1300°C.*

As shown in Figure D-5, red water treatment with the SRK technology would proceed as follows**:

1. Feeding of the red water into the rotary incinerator (primary incineration chamber).
2. High-temperature incineration of the red water (combustion gases enter the afterburner, and slag is removed).
3. Secondary combustion of gases in the afterburner.
4. Cooling of gases leaving the afterburner in either a quench tank or a steam boiler.
5. Scrubbing of gases to remove SO_x and some NO_x .
6. Further air treatment (if necessary) to reduce NO_x emissions through a Denox reactor or a selective catalytic converter.
7. Release of treated gas through a flue gas stack.

Rotary Kiln Incineration

The higher temperature of the SRK enables more complete combustion of the waste and encapsulation of constituents in the generated ash. Because the rotary kiln burns at a higher temperature than the melting point of salts contained in red water, the salts are removed from the kiln in a liquid form,

* Personal communication from R. Devin, Combustion Engineering, 1989.

** Personal communication from M. Kinkhabualala, Combustion Engineering, 1989.

DAAPES
2000

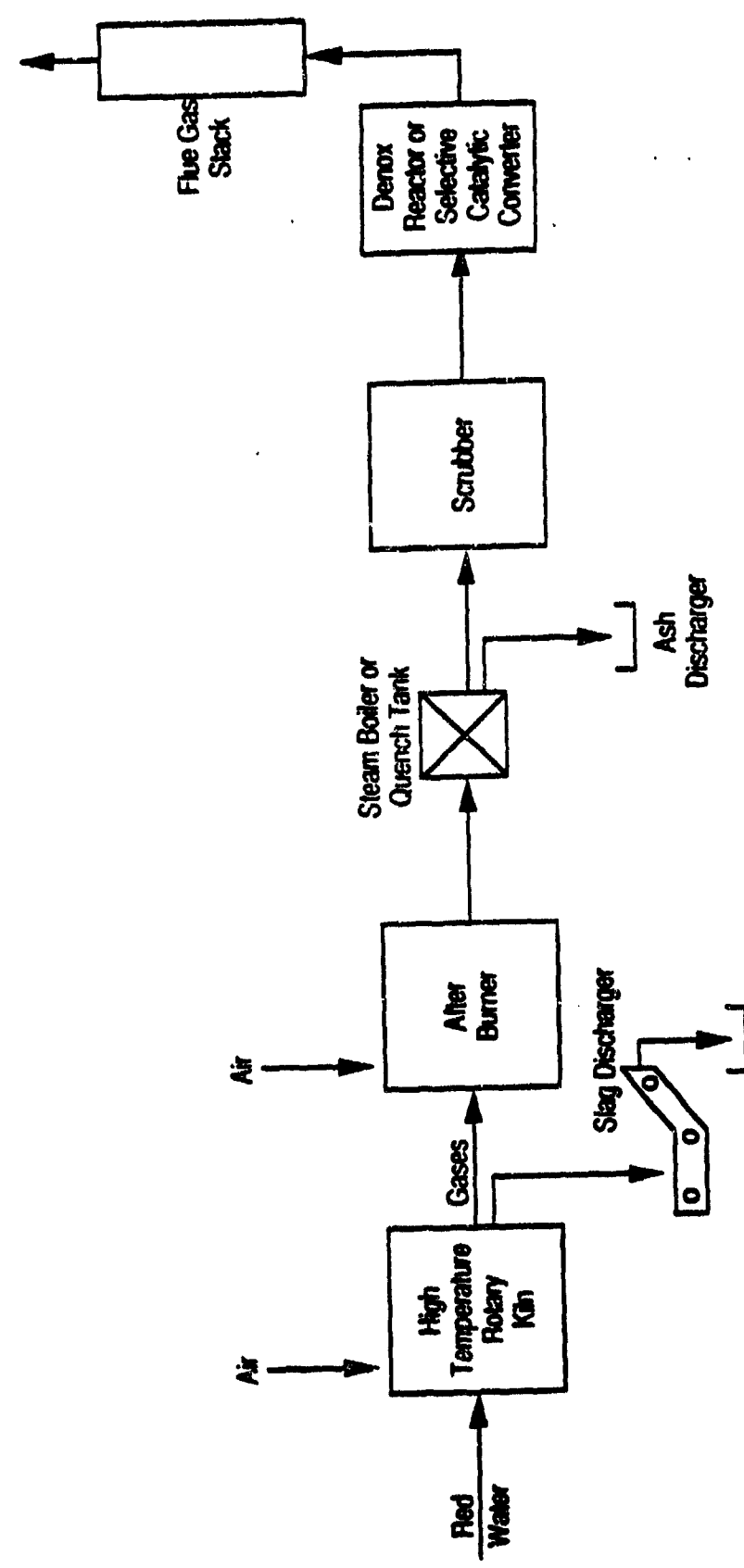


Figure D-5
PROCESS SCHEMATIC FOR TREATMENT OF RED WATER USING THE SLAGGING
ROTARY KILN TECHNOLOGY

source: merrill, 1982

HUNTER/EE
Secondary Evaluation of
Red Water Treatment Technologies

which results in less downtime than that required for conventional rotary kiln incineration.* Slag resulting from the SRK process is a molten material that forms an encapsulated solid when immersed in a water bath. In comparison with ash produced by standard incineration processes, the slag is much more resistant to leaching.** Sand may be added to the molten slag to produce a glassified waste when the mixture is cooled in a water bath.

Use of a water-evaporation system before the rotary incinerator can concentrate solids in the red water to an estimated 35 percent and may reduce overall costs of red water treatment. A lower water content in the red water entering the rotary incinerator can permit a smaller kiln to be used, and less fuel would be needed to maintain high temperatures.***

Rotary kiln operation is more economical at lower temperatures than at slagging temperatures. Also, the higher temperatures of the SRK shorten the refractory life significantly. Operating at lower temperatures has some disadvantages, however. The ash resulting from incineration at the lower temperatures is more likely to be leachable. In addition, salts contained in the ash produced at lower temperatures may adhere to the kiln; however, these salts could be cleaned out by periodically operating the kiln at slagging temperatures to melt the salts.

Secondary Combustion/Gas Treatment

The afterburner (or secondary combustion chamber) provides additional residence time in an excess-air environment for destruction of organic compounds in the gas stream. The afterburner generates hot combustion gases that must be cooled before entering the scrubbing system. Gases can be cooled in a quench tank or in a steam boiler. The quench tank saturates the gas stream with recirculated water, neutralizes some of the acids, and agglomerates and removes coarse particulates. The steam boiler generates steam, which results in cooling of the gas. The scrubber system removes inert organic and inorganic particulates from the gas stream. Nitrogen

* Personal communication from J. Delloiacovo, Combustion Engineering, 1989.

** Personal communication from R. Devin, Combustion Engineering, 1989.

*** Personal communication from M. Kinkhabuala, Combustion Engineering, 1989.

oxides present in the gas stream leaving the afterburner can be removed by using a Denox reactor or selective catalytic converter.*

Demonstrated Waste Treatment

The SRK technology has not been tested with red water. Commercial slagging rotary kilns have been used to burn a variety of mixed wastes in Europe and the United States. This technology has been used effectively for more than 10,000 types of wastes, including PCBs and steel drums containing liquid wastes,** and has achieved destruction and removal efficiencies of greater than 99.99 percent for most compounds tested. Destruction and removal efficiencies of 99.9999 percent have been achieved for PCBs.***

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The SRK technology has not been tested with red water; however, it has been used to treat many types of wastes. Destruction and removal efficiencies of greater than 99.99 percent were achieved for most compounds tested. The technology can be used to treat liquid wastes such as red water; however, much more efficient treatment is possible with wastes containing higher solids contents. Thus, the SRK technology may not be practical for treating red water because of its high water content.

Several data gaps and problem areas exist for an evaluation of the potential for effective red water treatment with the SRK technology. First, because the technology has not been tested with red water, its technical feasibility is somewhat uncertain. Nevertheless, the successful treatment achieved with numerous other wastes makes the potential for effective red water treatment good.

* Personal communication from M. Kinkhabualala, Combustion Engineering, 1989.

** Personal communication from R. Devin and J. Delloiacovo, Combustion Engineering, 1989.

*** Personal communication from J. Delloiacovo, Combustion Engineering, 1989.

Disadvantages of the SRK technology compared with standard incineration processes are as follows:

- ° Higher capital investment
- ° Greater energy costs
- ° Greater operation and maintenance costs
- ° Shorter refractory life*
- ° Extensive pretreatment requirements to increase the solids content of the wastewater.**

Current Application and Status of Technology

The SRK technology has been demonstrated on a full scale in the treatment of numerous solid and liquid wastes. Although the exact composition of the wastes tested is unknown, the technology has successfully treated most of these wastes.

Environmental Impact

Use of the SRK technology to treat red water is expected to meet most environmental requirements. Air emission requirements should be met if a scrubber and either a Denox reactor or a selective catalytic converter are used. Water used to cool gases generated in the afterburner is recirculated. Effluents from the quench tank and scrubber system must be characterized to determine the extent of treatment needed. The majority of the solid waste produced during the SRK process in a molten form that; when immersed in a water bath, however, they become an encapsulated solid that should be resistant to leaching.***

Time and Cost for Implementation

Implementation as a full-scale treatment of red water should be relatively simple because the technology has been used extensively for treatment

* Personal communication from J. Delloiacovo and M. Kinkhabuala, Combustion Engineering, 1989.

** Personal communication from R. Devin, Combustion Engineering, 1989.

*** Personal communication from M. Kinkhabuala, Combustion Engineering, 1989.

of other liquid wastes. The time involved for laboratory testing, pilot-plant testing, and design for treatment of red water by the SRK technology is estimated to be 2 to 6 months. The cost for testing and design may range from \$10,000 to \$200,000, depending on the extent of testing performed. The estimates of implementation time and costs do not include construction of the full-scale system.*

Based on an assumed treatment of 16,250 gallons of red water per day, the capital cost of an SRK system manufactured by Combustion Engineering is estimated to be \$12,000,000 (assuming 15 percent solids in the red water). If the red water has been pretreated in an evaporator to attain a 35 percent solids content, the estimated capital cost would be \$8,000,000. The O&M costs for the SRK system are estimated to be \$1500/1000 gallons of red water.*

Complexity, Operation, and Flexibility

Treatment of red water with the SRK technology is relatively complex. The unit processes include water evaporation (optional), high-temperature rotary kiln incineration, secondary combustion via an afterburner, and gas cleaning via a scrubber and NO_x reduction system. Laboratory and pilot-scale testing with red water will probably be required to assure an effective treatment system. The process has broad flexibility and a wide operating range.**

Evaluation Summary

The overall evaluation of the process is favorable because the technology has the potential of treating red water while meeting environmental requirements.

Table D-10 presents a quantitative evaluation of the technology based on five categories of evaluation criteria. The final score for the SRK technology is 68 of a possible 110 points.

* Personal communication from M. Kinkhabualo, Combustion Engineering, 1989.

** Personal communication from J. Delioiacovo, Combustion Engineering, 1989.

TABLE D-10. QUANTITATIVE EVALUATION OF SLAGGING ROTARY KILN

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	9
2. Current application and status of technology	14
3. Environmental impact	25
Wastewater discharge regulations	6
Air emission regulations	6
Solid/hazardous waste regulations	13
Recyclability	0
4. Time and cost for implementation	8
Time	4
Cost	4
5. Complexity, operation, and flexibility	12
Process complexity	3
Difficulty of operation	3
Flexibility of operating parameters	3
Miscellaneous	3
TOTAL	68

SUBMERGED COMBUSTION PROCESS

TECHNOLOGY DESCRIPTION

Background

Submerged combustion is a thermal treatment technology that uses a liquid injection slagging furnace for destruction of aqueous organic wastes. The difference between this process and conventional liquid-injection incineration processes is the temperature at which waste is burned. In submerged combustion, liquid waste is introduced to the furnace, where it is burned at a temperature high enough to melt salts that are formed in the process. An auxiliary fuel is used to sustain combustion. The amount of fuel required is mainly a function of the liquid flow rate (i.e., waste flow) into the treatment unit and the heat value (i.e., Btu/lb) of the waste. Because the processing temperature exceeds the melting point of the newly formed salts, the molten salts can be easily removed from the furnace. This process minimizes salt buildup and fouling. The molten salt is drained into a water bath, which yields a highly saline solution that can be discharged to a wastewater treatment facility or be dried to form a salt cake. As in most incineration processes, the effluent gases may require particulate removal, acid gas neutralization, and NO_x and SO_x reduction (Foster Wheeler 1988).

Representatives of Envirospan have indicated that the submerged combustion process is capable of a 99.99 percent reduction of many organic compounds (Foster Wheeler 1988). Treatment of red water with the submerged combustion process has not yet been investigated; therefore, the treatment of red water in the submerged combustion process is strictly conceptual at this time. A submerged combustion test facility is available for the evaluation of red water treatment. Envirospan representatives have indicated that red water testing at the manufacturer's test facility could generate the necessary data for delisting byproducts from the process.

Process Flow Description

Figure D-6 is a flow diagram of the submerged combustion process. The process flow description is summarized as follows (T-Thermal 1989):

1. The incinerator chamber is usually vertical, and the burner is near the top of the chamber. Finely atomized combustible waste is mixed with combustion air and injected into the flame zone just below the burner. Resulting molten salts flow down the refractory wall to the quench chamber. Temperature is extremely critical; the optimum level ranges from 850° to 1000°C.
2. Hot gases pass through a water-cooled downcomer tube and are quenched in the quench tank. The quench bath will recover approximately 90 percent of the particulates.
3. Process heat can be recovered to preconcentrate incoming aqueous waste.
4. An off-gas scrubbing system will be necessary to remove SO_x and NO_x from the gas phase prior to the discharge of gases.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Based on the process flow description presented in the preceding subsection, the submerged combustion process has a high theoretical potential for treating red water. Most organics can be completely eliminated in the process because of the high operating temperatures in the combustion chamber. The process is also well suited for organic wastes in aqueous solutions (T-Thermal 1989).

Current Application and Status of Technology

The submerged combustion process is currently being used at approximately 116 different locations around the world.* Evaluation of red water or wastes similar to red water, however, have not been evaluated on any scale or in theoretical studies. Although the process embodies the intrinsic capability to treat red water, it cannot be stated with any degree of certainty that it will be successful in such an application.

* Personal communication from G. Irrgang, T-Thermal, Inc., 1989.

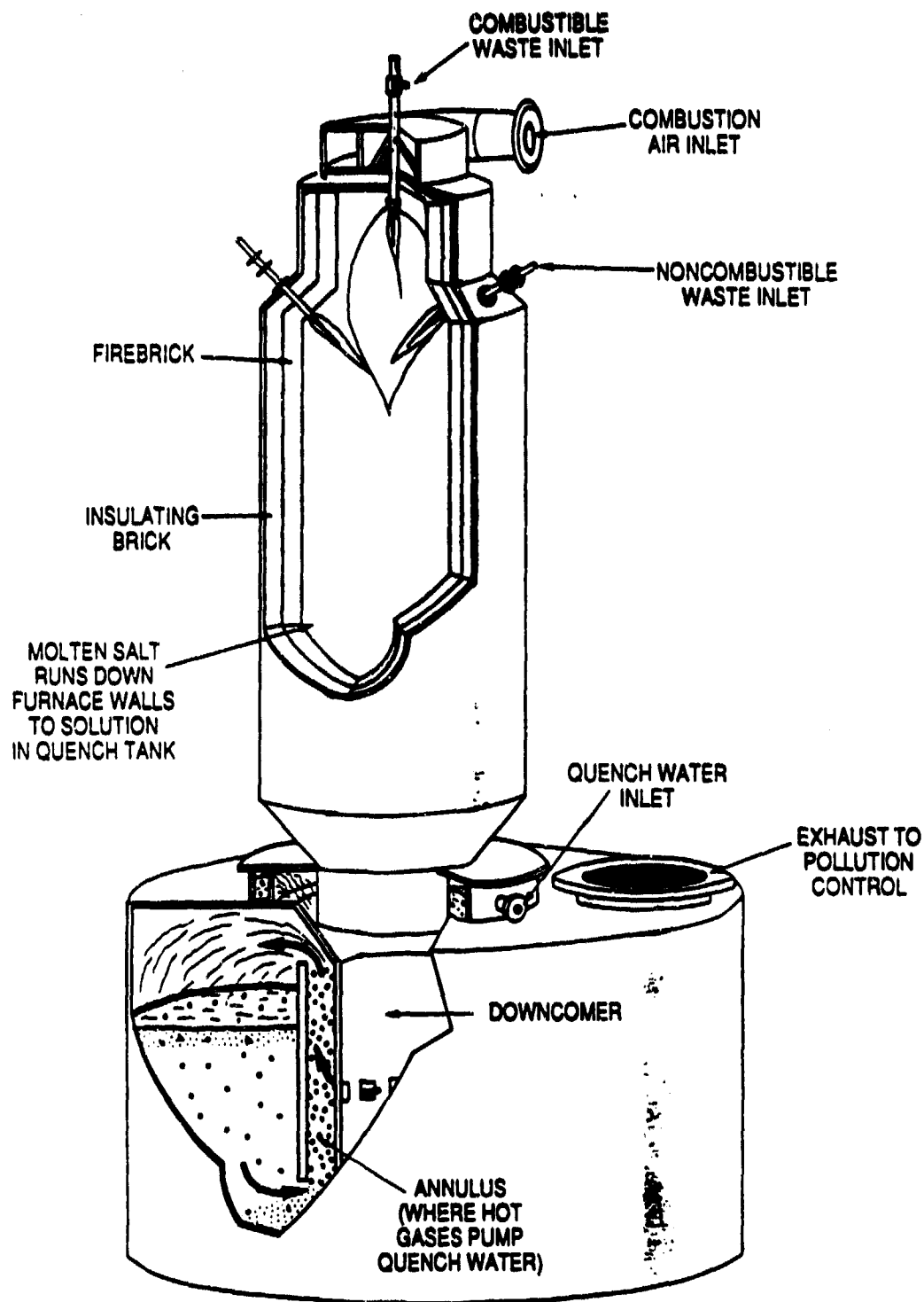


Figure D-6
SUBMERGED COMBUSTION TREATMENT UNIT
T-THERMAL VORTEX BURNER ASSEMBLY

SOURCE: T-THERMAL, 1988.

HUNTER/ESE

Secondary Evaluation of
Red Water Treatment Technologies

Environmental Impact

Wastewater Discharge Regulations--

Two wastewaters are generated by the process: 1) scrubber water from the air pollution control equipment, and 2) water from the quenching bath. The scrubber water is expected to contain SO_x , NO_x , and particulates, which are released to the gas phase. Because of the high operating temperature of the process, salts formed upon combustion will be in a molten state. Before the salts can cool and form into slag, they will be quenched in a water bath, which will yield a brine solution instead of the slag generally produced in other thermal treatment processes. Both the quenching solution and water from the scrubbers are expected to meet discharge standards with conventional physical/chemical treatment processes.

Air Emission Regulations--

The effluent gases resulting from treatment of red water will probably require particulate removal, acid gas neutralization, and NO_x and SO_x reduction. Air discharged from pollution control devices is expected to meet discharge standards.

Solid/Hazardous Waste Regulations--

Liquid wastes from the process will probably require onsite treatment, as described previously. Assuming the residuals from the treatment process (i.e., quench water) can be delisted, the onsite treatment process will not require an operating permit for treatment of hazardous wastes, and residuals from this treatment process will be considered nonhazardous industrial wastes. The quench water may also be evaporated to form a salt cake. If the residuals from the evaporation process can be delisted, the dried salts could be disposed of as a nonhazardous waste.

Recyclability--

Salt residuals from the process are in a form that makes them undesirable for recycling. Recycling of water from the quenching bath and air pollution control system for reuse in the TNT purification process will probably not be economical. Therefore, no portion of red water is expected to be recycled for use in TNT production or purification.

Time and Cost for Implementation

T-Thermal, Inc., has a 1-million-Btu pilot plant that can be used for testing treatment of red water. Results from pilot tests with the submerged combustion process could be used to assess the effectiveness of red water treatment and to define design parameters for a full-scale process. Pilot-scale tests could be completed in a period of 3 months, including the time for setup, testing, and reporting. Costs of the pilot test are estimated to be \$20,000 to \$80,000. Design of a full-scale unit could proceed after the pilot tests. A full-scale design could be completed in approximately 12 months at an estimated cost of \$300,000. Therefore, the total time to implementation of the treatment technology is estimated to be 15 months, and the cost is estimated to be \$320,000 to \$380,000. These time and cost estimates do not include procurement of equipment, construction, or installation of the treatment unit.

Capital costs for the engineering and installation of the submerged combustion and wastewater treatment units are estimated to be \$2 million.

Operation and maintenance costs involve consumption of electricity and fuel oil, labor, treatment of wastewater, replacement of refractory, and miscellaneous items. Assuming 16,250 gallons of red water will be treated per day on a continuous basis, the approximate cost for treatment is estimated to be \$100/1000 gallons.

Complexity, Operation, and Flexibility

For evaluation of the complexity, ease of operation, and flexibility, the full-scale submerged combustion process is assumed to have a capacity of 24 to 30 million Btu per hour. Wastewaters generated by the process are assumed to be treated through an ion-exchange (I/E) treatment unit (consisting of anion and cation exchange), and regenerant solutions resulting from reactivation of ion-exchange resins are assumed to be disposed of as a nonhazardous liquid waste.

Process Complexity--

Submerged combustion--The process is relatively simple. The only feeds to the process would be red water, auxiliary fuel, and air. Auxiliary fuel

and air feeds to the process will have to be adjusted as the composition of red water changes. Combustion is achieved early in the process, and the remainder of the process is devoted to scrubbing off-gases and quenching molten salt combustion products.

Ion-exchange--Ion-exchange is a relatively simple treatment process. Particulates from the quench solution and scrubber water would have to be removed (e.g., sand filtration) prior to I/E treatment of wastewaters. Periodic monitoring of effluent from the I/E treatment unit by use of simple chemical analysis would be required to monitor the exhaustion of the I/E resin. The pH of the influent and effluent around the I/E process may have to be adjusted to make effective use of resins and to meet discharge standards.

Difficulty of Operation--

Submerged combustion and ion-exchange--One full-time operator per shift will be required to maintain both treatment processes. The processes are not considered difficult to operate as long as a well-trained experienced operator is overseeing the treatment system. Periodic analysis of red water will be necessary to help define air and fuel requirements for cost-efficient combustion.

Flexibility of Operating Parameters--

Submerged combustion--The operating parameters are relatively inflexible. The addition of auxiliary fuel to the process will be dictated by the composition and flow rate of the red water into the treatment process. Operating temperature is critical to ensure complete combustion of red water.

Ion-exchange--The I/E process is flexible. Control of solids and pH will be required to minimize fouling of resins. A minimum hydraulic contact time must be maintained within the I/E adsorption contactor. If the system is designed to treat a maximum flow rate and contact time for the removal of ions is acceptable at the design capacity, lower flow rates of wastewater can be processed through the unit without any modifications to treatment or reductions in effluent quality.

Miscellaneous--

Submerged combustion--The treatment process has a strong theoretical potential for treatment of red water. Although the process embodies the

intrinsic capability to treat red water, it cannot be stated with any degree of certainty that the treatment of red water will be successful. The process is in widespread use around the world and is proven on a full scale for treatment of organic waste liquids. Two drawbacks to the process are 1) most of the fuel feed is required solely to evaporate water, and 2) the process generates both wastewater and gases that must be treated before discharge.

Evaluation Summary

Table D-11 presents a quantitative evaluation of the submerged combustion technology based on five categories of evaluation criteria. The final score for the submerged combustion process is 66 of a possible 110 points.

TABLE D-11. QUANTITATIVE EVALUATION OF THE SUBMERGED COMBUSTION PROCESS

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	9
2. Current application and status of technology	14
3. Environmental impact	25
Wastewater discharge regulations	6
Air emission regulations	6
Solid/hazardous waste regulations	13
Recyclability	0
4. Time and cost for implementation	8
Time	4
Cost	4
5. Complexity, operation, and flexibility	10
Process complexity	2
Difficulty of operation	3
Flexibility of operating parameters	2
Miscellaneous	3
TOTAL	66

SUPERCritical WATER OXIDATION

TECHNOLOGY DESCRIPTION

Background

Supercritical water oxidation (SCWO) is a process in which organic compounds are oxidized to inorganic compounds. The fundamental difference between SCWO and conventional oxidation processes is the physical state at which the material is maintained prior to the initiation of the oxidation reaction. In the SCWO process, a liquid is subjected to extreme temperatures (above 374°C) and pressures (above 212 atmospheres) that elevate the liquid to a state at which water is defined as supercritical. Oxygen is an effective oxidant at this state in which gases and liquids are indistinguishable. In comparison with conventional oxidation processes, this process is more efficient because the oxygen is introduced at a condition that optimizes oxidation kinetics (Foster Wheeler 1988).

The application of this process for the oxidation of waste organic materials requires moderate- to high-pressure reactor vessels, efficient heat exchange, the ability to dissolve stoichiometric oxygen into the reaction vessel, and sufficient heating value (Btu/lb) of the organic waste stream to support the heat losses of the process. When toxic or hazardous organic chemicals are subjected to the SCWO process, carbon is converted to carbon dioxide and hydrogen is converted to water. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitrogen compounds produce nitrogen gas, sulfur is converted to sulfates, and phosphorous is converted to phosphates (Foster Wheeler 1988).

Two vendors, MODAR and Oxidyne, have been identified as manufacturers of SCWO processes (Foster Wheeler 1988). The MODAR system operates as a closed system that is self-scrubbing. This process uses pure oxygen and may require an auxiliary fuel if the wastes to be destroyed do not contain sufficient heating value to support heat losses to the process. With this process,

emission controls are not needed because the inorganic contaminants remain in the liquid phase (Foster Wheeler 1988). Theoretical and bench-scale tests performed by MODAR defined destruction efficiencies for eight groups of compounds. Results of these 1985 pilot tests are as follows (Foster Wheeler 1988):

<u>Contaminant</u>	<u>Destruction efficiency</u>
2-Chlorophenol	>99.997
Nitrobenzene	>99.998
1,1,2-Trichloroethene	>99.981
Chloroform	>99.83
Carbon tetrachloride	>96.53
Polychlorinated biphenyl	>99.9949

Treatment of red water with the MODAR SCWO process has not been investigated; therefore, treating of red water with this process remains strictly conceptual. Based on a materials balance and thermodynamic modelling of red water treatment in the MODAR process, carbon dioxide and nitrogen would be the only compounds expected to be released in the off-gases. Sodium sulfate is the only compound expected to be present in the wastewater generated by this process (Foster Wheeler 1988).

The principal differences between the Oxidyne process and the MODAR system are in the reaction configurations. The Oxidyne process provides an alternative to above-ground processes by using 10,000 to 12,000 ft of natural hydrostatic head, which is attained in deep-well reactors. As in the MODAR process, the Oxidyne process uses pure oxygen and may require an auxiliary fuel if the wastes to be destroyed do not contain sufficient heating value to support heat losses to the process. Literature on the Oxidyne process presented by Foster Wheeler (1988) indicates destruction efficiencies ranging from 99.99 to 99.9999 percent. The only data available for this system, however, were from tests performed with sewage sludge in a 1500-ft reactor, which resulted in the removal of more than 80 percent of the chemical oxygen demand. Whether any testing has been performed on wastes containing hazardous organics is not known (Foster Wheeler 1988).

Process Flow Description

Figure D-7 presents the process flow diagram for the MODAR SCWO process. The process flow description is summarized as follows (Foster Wheeler 1988):

Feed--

- 1) Organic waste in an aqueous medium is pumped from atmospheric pressure to the pressure in the reaction vessel.
- 2) Oxygen, stored as a liquid, is pumped to the pressure of the reaction vessel and then vaporized.
- 3) Feed to the process is controlled to an upper heating value limit of 1800 Btu/lb by adding dilution water or by blending high-heating-value waste material with a lower-heating-value waste material prior to the reactor.
- 4) When the aqueous waste has a heating value below 1800 Btu/lb, fuel may be added for use as a cold feed to the oxidizer.
- 5) Optionally, when wastes have a heating value below 1800 Btu/lb, a combination of preheat by exchange with process effluent and fuel addition or preheat alone may be used.
- 6) When organic wastes containing elements that produce mineral acids (heteroatoms) are present in the waste and neutralization of these acids is desired, caustic is injected as a part of the feed stream, which yields salts.
- 7) A recycle stream of a portion of the oxidized effluent is mixed with the feed stream to raise the combined fluids to a high temperature to ensure that the oxidation reaction proceeds rapidly to completion.

Reaction and Salt Separation--

- 1) Because water is above its critical point, the oxidant is completely miscible with the solution (i.e., the mixture is a single homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Because the oxidizer operates adiabatically, the heat released by the readily oxidized components is sufficient to raise the fluid to temperatures at which all organics are oxidized rapidly.
- 2) Because the salts have very low solubility above critical temperatures, they separate from the other homogeneous fluid and fall to the bottom of the separation vessel, where they are removed.
- 3) The gaseous products of reaction, along with the water, leave the reactor at the top. A portion of the fluid is recycled to the



Figure 2. PROCESS SCHEMATIC FOR SUPERCRITICAL WATER OXIDATION OF RED WATER

SOURCE: FOOTER WHEELER, 2001.

HUNTERVESE

Secondary Evaluation of Red Water Treatment Technologies

oxidizer by a high-temperature, high-pressure pump. This operation heats the feed sufficiently to bring the oxidizer influent to optimum reactor conditions.

- 4) The remaining reactor effluent (other than that recycled), which consists of superheated water and carbon dioxide, is cooled to permit the discharge of carbon dioxide and water at atmospheric conditions.

Cooling and Heat Recovery--

- 1) Most of the heat contained in the effluent can be used to generate steam for use outside the process.
- 2) The heat remaining in the effluent stream is used for lower-level heating requirements and is also dissipated.

Pressure Letdown--

- 1) The cooled effluent from the process separates into a liquid water phase and a gaseous phase containing primarily carbon dioxide and oxygen in excess of the stoichiometric requirements.
- 2) The separation is carried out in multiple stages to minimize erosion of valves and to optimize equilibria.
- 3) Salts are removed from the separator as a cool brine through multiple letdown stages and are either dried (and water recovered) or discharged as a brine.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Based on the process flow description presented in the preceding subsection, SCWO has a high theoretical potential for treating red water. Control of the pH of the feed stream will be necessary, however. Under acidic conditions, reduction and diazotization of the 4-nitro group in 2,4-DNT-5-SO₃Na was believed to result in the formation of an explosive compound, which was isolated during experiments on red water destruction by the acidification process (Eckenrode, Densler, and Klein 1980). Because SCWO oxidation involves heating and because mineral acids may develop in the process, caustic should be added to minimize the possibility of forming the explosive compound discovered in earlier testing.

Current Application and Status of Technology

Removal efficiencies for selected organic compounds were listed earlier. In MODAR's early testing of the process for treatment of a 12 percent DNT solution in methyl ethyl ketone, DNT measurements were not made after treatment; however, a mass balance of organic carbon indicated a total organic carbon destruction efficiency of 99.99 to 99.999 percent, which indicates significant destruction of DNT in the bench-scale treatment study.* Efforts were made to measure NO_x and SO_x emissions during testing, but the data were inconclusive.

Currently, MODAR does not have a full-scale process in operation, but they expect to have one operating by the end of 1990. Whether Oxidyne has a full-scale process in operation is not known. Therefore, the full-scale application of this treatment technology remains conceptual at this time, and the reliability of the process is uncertain. Because red water has not been tested in bench-scale or pilot-scale testing, the application of SCWO for this purpose remains strictly conceptual. Problems associated with scale-up from pilot scale to full scale are probable.

Environmental Impact

Wastewater Discharge Regulations--

After the salt separator, water from the treatment process may be discharged to a publicly owned treatment works. If effluent from the process must be discharged to a ground-water reinjection well or to surface water, however, additional treatment may be necessary to remove soluble salts.

Air Emission Regulations--

Upon oxidation of sulfur groups, sulfate will form and remain in the solution as a soluble salt or precipitant. Nitrogen groups may be oxidized to NO_x , nitrous oxide, and nitrogen gas; therefore, a pollution control device for removal of NO_x will probably be necessary. The production of NO_x and nitrous oxide can be eliminated by maintaining the operating temperature of the process at approximately 650°C.

* Personal communication with G. Hong, MODAR Inc., 1989.

Solid/Hazardous Waste Regulations--

The salts generated by the separation of salt precipitants and water must be disposed of. These salts are not expected to exhibit characteristics of a hazardous waste. Therefore, assuming the residuals from the treatment process can be delisted, the salts can be disposed of in a nonhazardous industrial landfill.

Recyclability--

After the treatment, all the water generated as effluent from the treatment process can be repeatedly reused in the process. The SCWO process will also generate residual steam that can be used for other purposes at the facility. Salt residuals from the treatment process are in a form that make them undesirable for recycling.

Time and Cost for Implementation, Capital and O&M Costs

MODAR has a bench-scale testing unit which can be utilized to assess the effectiveness of red water treatment in the SCWO process. Results from bench-scale tests can be utilized to define design parameters for a full-scale treatment process. Pilot tests and design of the full-scale unit can be completed within a 12-month period. The costs for testing are estimated to be \$50,000 to \$75,000. Design costs are estimated to be \$600,000. Therefore, it is estimated that the time to implementation of the treatment technology would be approximately 12 months and would cost approximately \$650,000 to \$675,000. This cost and time estimate does not include procurement of equipment, construction, or installation of the designed treatment unit.

Capital costs are estimated to be \$6 million for the engineering and installation of the treatment process. Because a full-scale treatment has not been installed, however, the accuracy of this estimate is questionable.

Operation and maintenance costs, which involve continuous consumption of electricity, fuel oil, labor, oxygen, caustic, and other miscellaneous items, are estimated to be \$1.3 million per year. Assuming 16,250 gallons of red water will be treated per day on a continuous basis, the estimated cost for treatment is \$220/1000 gallons.

Complexity, Operation, and Flexibility

Process Complexity--

The process is relatively complex because of the high operating temperatures and pressures required for destruction of organic compounds. Also, four different feeds (see process flow diagram) are necessary for treatment of red water and must be constantly monitored.

Difficulty of Operation--

For the reasons described previously, one full-time operator per shift will be required. Although the process will require full-time attention, operation of the process should not be difficult if the operator is well trained and experienced.

Flexibility of Operating Parameters--

The operating parameters for destruction of red water will not be flexible. A minimum pressure and specific temperature will be required for operation. If the pressure and temperature are not maintained at the proper levels, insufficient treatment and generation of excess NO_x emissions are likely.

Miscellaneous--

The process has a strong theoretical potential for treatment of red water; however, the estimated capital and O&M costs are very high. Also, because the process has yet to be proven on a full scale, the accuracy of capital and O&M costs is questionable.

Evaluation Summary •

Table D-12 presents a quantitative evaluation of the SCWO technology based on the five categories of evaluation criteria. The final score for the SCWO process is 51 of a possible 110 points.

TABLE D-12. QUANTITATIVE EVALUATION OF SUPERCRITICAL WATER OXIDATION

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	6
2. Current application and status of technology	10
3. Environmental impact	25
Wastewater discharge regulations	5
Air emission regulations	8
Solid/hazardous waste regulations	12
Recyclability	0
4. Time and cost for implementation	5
Time	3
Cost	2
5. Complexity, operation, and flexibility	5
Process complexity	1
Difficulty of operation	2
Flexibility of operating parameters	1
Miscellaneous	1
TOTAL	51

THERMAL SEPARATION

TECHNOLOGY DESCRIPTION

Background

Thermal separation, developed by International Technology Corporation (IT), is a process in which wastes containing organic contaminants are treated in an indirectly heated thermal separator unit at temperatures high enough to vaporize the organic components. The organic vapors from the unit are discharged in the off-gas, which is treated by either fume incineration or condensation/scrubbing. A similar technology, low-temperature thermal treatment, has been developed by Weston Services, Inc. Temperatures used in both of these technologies are lower than those used in standard incinerators. Because heating is indirect, the volume of gaseous materials leaving the separator unit is smaller than in standard incinerators (Fox 1988).

The IT thermal separation technology has been demonstrated on pilot- and full-scale systems for treatment of soils and solids contaminated with organic contaminants, including PCBs, PCDDs, PAHs, chlorinated solvents, petroleum hydrocarbons, and pesticides (Fox 1988). The Weston low-temperature thermal treatment technology has been demonstrated on pilot- and full-scale systems for treatment of soils and solids contaminated with chlorinated solvents and petroleum hydrocarbons. The technologies have not been tested on liquid wastes in general or on red water specifically (Nielson and Cosmos 1988).

For the treatment of red water by thermal separation, IT representatives have proposed using a rotary calciner as the thermal separation device. The rotary calciner, which is made of an indirectly heated metal alloy, is capable of processing solids at temperatures up to 600°C. The calciner has been used for thermal decomposition of the nitrate salts of radioactive materials in aqueous solutions. The nitrogen oxide gases are recovered as nitric acid, and the radioactive oxide solids are left for waste disposal. If nitrobody-free sodium sulfate cannot be produced cost-effectively in the calciner, a second treatment stage consisting of incineration in a small rotary kiln

could be used to achieve the desired performance. Gases leaving the calciner will contain NO_x , steam, and decomposed organics. The gases could be treated in a system that first condenses the steam and most of the organics, and in which the NO_x are collected in a scrubbing system for the recovery of nitric acid. Any noncondensable organics could be treated in a fume incinerator. The condensed water and organics would be treatable by conventional means such as biological oxidation. Figure D-13 presents a flow diagram of the treatment process (Fox 1988).

Advantages of thermal separation compared with rotary kiln incineration are as follows:

1. A low volume of gas is produced in the calciner, which enables recovery of NO_x as nitric acid by use of scrubbing technology.
2. Oxidized organics are discharged from the device either in the water condensate (which is subsequently treated by conventional treatment) or in the low-volume noncondensable gases (which are treated by fume incineration).
3. The calciner surface, constructed of a specially fabricated metal alloy, can withstand direct injection of the red water onto the hot surfaces.
4. Operating temperatures can be adjusted to below the softening/fusion points of the salts produced.

Byproducts of the technology include acidic condensate water, which results from the gas treatment system, and a solid residue, which results from the thermal separator unit (Fox 1988). Although this residue should consist primarily of sodium sulfate, the ash will also contain any organics that were not removed from the raw waste stream through evaporation or oxidation.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The rotary calciner used in thermal separation has been used widely in the thermal processing of various materials; however, the process has not been tested with liquid wastes or wastes similar to red water. Although the process will evaporate water from aqueous wastes, it is not practical for

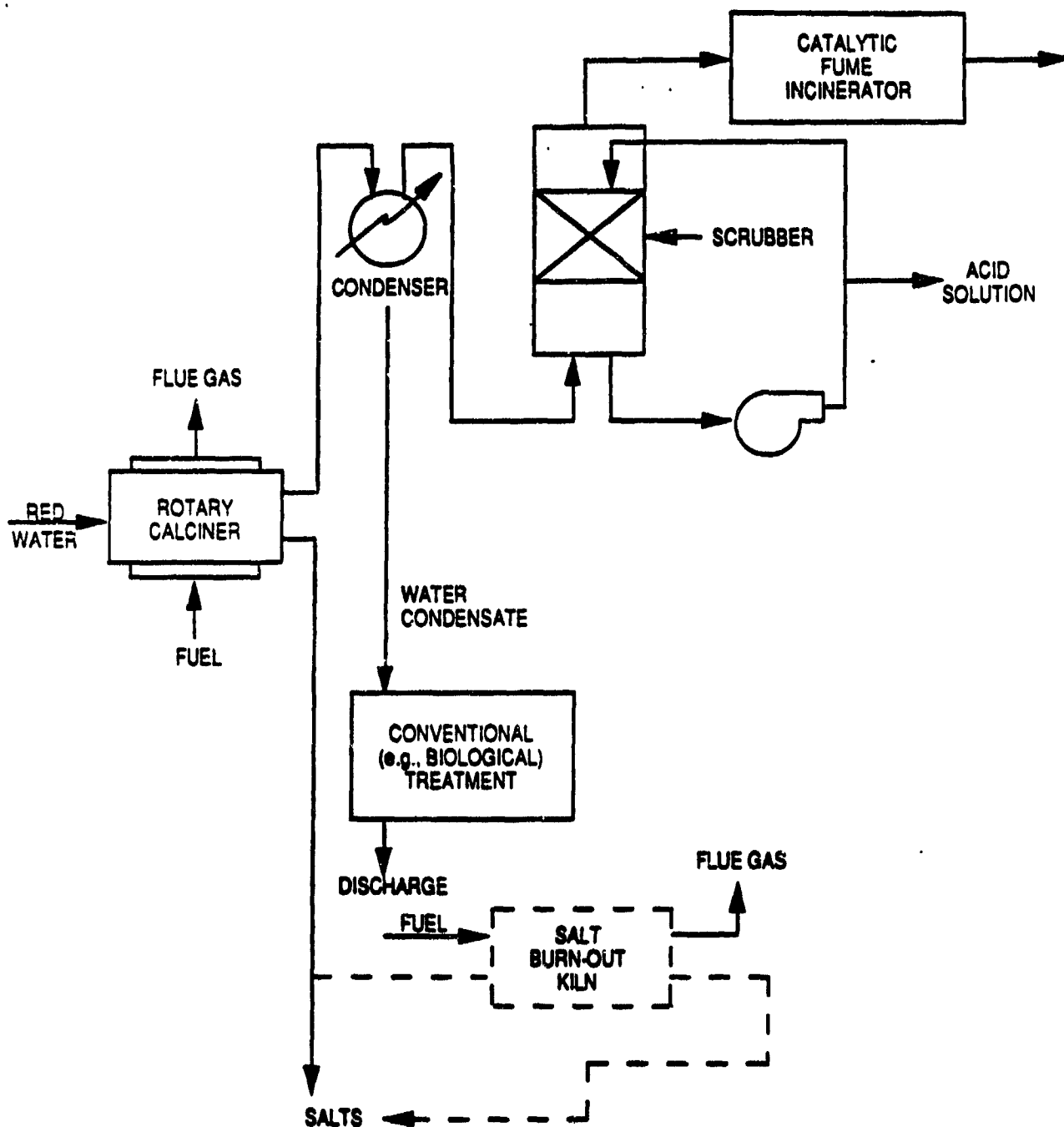


Figure D-8
PROCESS SCHEMATIC OF THERMAL SEPARATION
TECHNOLOGY FOR RED WATER TREATMENT

SOURCE: IT, 1988.

HUNTER/ESE

Secondary Evaluation of
Red Water Treatment Technologies

use on a waste such as red water, which contains approximately 85 percent water.* Therefore, the potential for using this technology to treat red water is limited.

Significant data gaps exist for the evaluation of the treatment of red water by thermal separation. The technology has not been tested on red water specifically or liquids in general. Therefore, the technical feasibility of treatment of red water by thermal separation is quite uncertain. Because this system is not designed to treat aqueous wastes, significant modifications would be required for its use in red water treatment.

Several problems could occur if the thermal separation technology were used to treat red water. After evaporation of the water, solids could adhere to the calciner and cause operational problems. Also, corrosion problems could develop when red water is added to the calciner.* Another problem involves disposal of the solid residue resulting from the process. Contaminants could leach from this sodium sulfate ash.

Current Application and Status of Technology

Thermal separation has been demonstrated on pilot- and full-scale systems for treatment of contaminated soils and solids. The process has been demonstrated at bench scale on soils contaminated with DDT, tetraethyl lead, kerosene, PCBs, PCDDs, PAHs, chlorinated solvents, petroleum hydrocarbons, and pesticides. On an engineering scale, IT has demonstrated thermal separation on Herbicide Orange chemicals, dioxins, PCBs, and furans. The technology has not been tested on red water or similar compounds (Helsel et al., undated).

Environmental Impact

If thermal separation can be used to treat red water, most environmental requirements should be met, with the possible exception of ash management. The expected decomposition of nitrate/nitrite salts in the calciner will produce a solid ash product of sodium sulfate. If calciner conditions of time and temperature cannot cost-effectively produce nitrobody-free sodium sulfate, a second stage of treatment of the sodium sulfate at higher

* Personal communication from R. Novak, International Technology Corporation, 1989.

temperatures in a small rotary kiln could be used to achieve the desired performance. The gases leaving the calciner (NO_x , steam, and decomposed organics) will be condensed and collected in a scrubbing system where nitric acid will be recovered. The resultant ash will be water-soluble and may contain impurities that could leach if disposed of on land. Any noncondensable organics will be handled in a fume incinerator. The condensed water and organics should be treatable by conventional means, such as biological oxidation (Fox 1982).

Time and Cost for Implementation

The costs for treating red water by the thermal separation process are not included in this report. Because treatment of an aqueous waste with thermal separation appears to be infeasible, the costs of an effective treatment system cannot be derived.

Complexity, Operation, and Flexibility

Thermal separation treatment of red water would be relatively complex, and the technology would be difficult to operate for several reasons. First, it has not been demonstrated for the treatment of aqueous wastes, so unexpected operational problems in waste handling could arise. Second, the process involves several operating steps entailing flash evaporation (and potentially a second stage of treatment of sodium sulfate in a small rotary kiln), treatment of gases through condensation and scrubbing, and treatment of condensed water. Significant pilot-scale testing with red water would probably be required. Established operating parameters for red water treatment will not be very flexible because they must be closely maintained to provide adequate treatment of the waste. If at all feasible, full-scale implementation of the thermal separation technology for red water treatment may be extremely difficult because the process has not been demonstrated with liquids.

Evaluation Summary

The overall evaluation of the process is unfavorable for the following reasons: 1) the process is not demonstrated for aqueous waste treatment or treatment of wastes similar to red water; 2) the potential exists for severe

operational problems associated with the use of thermal separation with red water treatment; 3) extensive pilot-scale testing, as well as design analysis, would be required prior to red water treatment; 4) O&M costs are expected to be relatively high because of the high water content of the red water; and 5) implementation is expected to be difficult because of data gaps. Based on this analysis, thermal separation is not recommended for red water treatment.

Table D-13 presents a quantitative evaluation of the thermal separation technology based on five categories of evaluation criteria. The final score for thermal separation is 43 of a possible 110 points.

TABLE D-13. QUANTITATIVE EVALUATION OF THERMAL SEPARATION TECHNOLOGY

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	3
2. Current application and status of technology	12
3. Environmental impact	22
Wastewater discharge regulations	8
Air emission regulations	4
Solid/hazardous waste regulations	10
Recyclability	0
4. Time and cost for implementation	2
Time	1
Cost	1
5. Complexity, operation, and flexibility	4
Process complexity	2
Difficulty of operation	1
Flexibility of operating parameters	1
Miscellaneous	0
TOTAL	43

CIRCULATING-BED COMBUSTION

TECHNOLOGY DESCRIPTION

Circulating-bed combustion (CBC) is a proprietary thermal treatment technology marketed by Ogden Environmental Services. The principal difference between CBC and the more traditional fluidized-bed technology is that CBC involves the introduction of air at much higher velocities (generally 15 to 20 feet per second), which causes waste particles to be suspended in the combustion gases. These highly turbulent conditions promote efficient combustion of organics, which reduces the required residence times and allows for more compact facilities compared with fluidized-bed incineration.*

Process Description

Figure D-9 presents a process schematic of the CBC process. The combustion chamber of CBC units currently in operation is 30 ft high, has a 36-in. inside diameter, and contains a 12-in.-thick ceramic liner. Air and auxiliary fuel (if needed) are injected at the bottom of the combustion chamber at high enough velocities to suspend the feed particles in the combustion gases. These velocities are higher than those used in fluidized bed reactors. Lower-density solids carried out in the gases from the combustor are removed in a cyclone separator and returned to the combustion chamber. This combustion loop operates at a nearly uniform temperature of between 800° and 1000°C. If solid wastes or feeds are used, these materials enter the loop where solids are returned from the cyclone to the combustion chamber. Liquid and sludge feeds are injected directly into the combustion zone of the CBC. Upon entering the CBC, hazardous materials are rapidly heated and maintained at operating temperatures. Residence times range from 2 seconds for gases to 30 minutes or longer for larger feed materials such as soils. The unit operates at subatmospheric pressure, which prevents the leakage or escape of hazardous materials in case of emergency shutdown.

* Personal communication from R. Haney, Ogden Environmental Services, 1989.

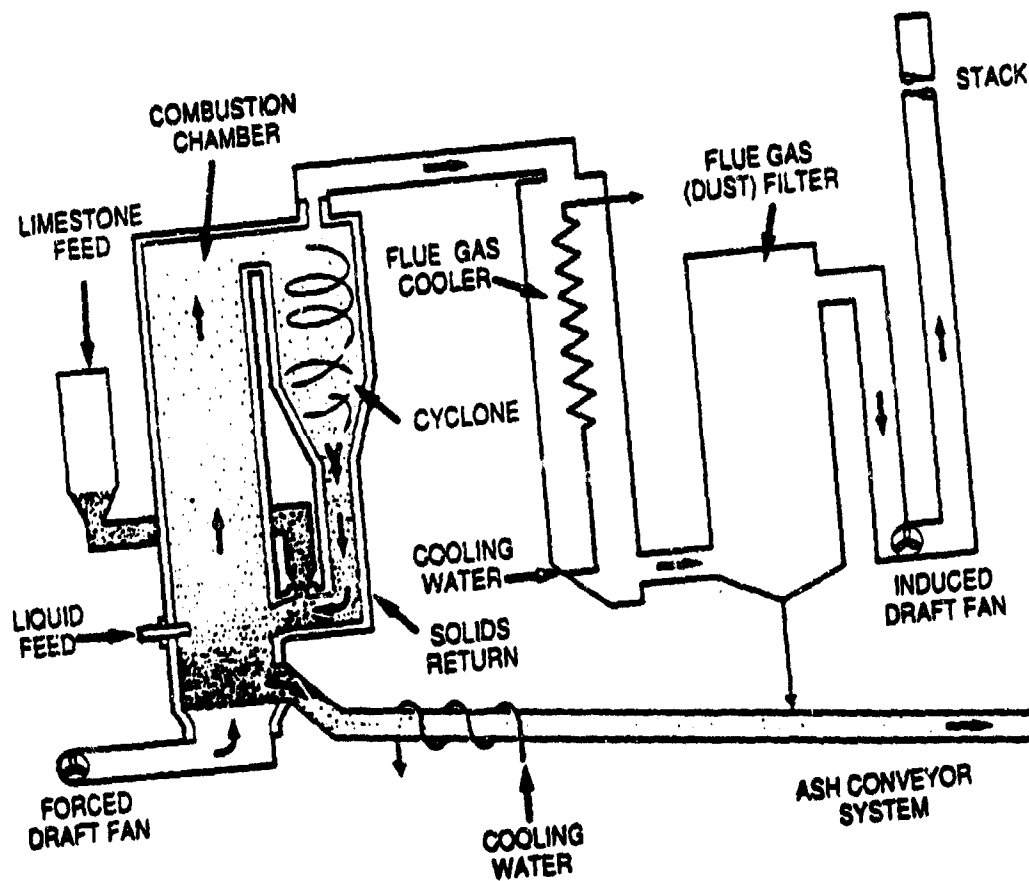


Figure D-9
PROCESS SCHEMATIC FOR CIRCULATING BED
COMBUSTION OF RED WATER

SOURCE: DOT, 1988.

HUNTER/ESE

Secondary Evaluation of
Red Water Treatment Technologies

Two major advantages of this technology over many other thermal treatment technologies are as follows:

- 1) Very efficient combustion eliminates the need for a downstream after burner.
- 2) Because of the high turbulence, the unit performs dry scrubbing in the combustor itself.

Ash is periodically removed during CBC operations by means of a water-cooled ash removal system. Hot gases leaving the top of the cyclone are cooled in a flue gas cooler, and particulates that escape are collected in a fabric filter system.

When the CBC is used to treat liquid wastes, atomizing is not needed. Instead, wastes are simply injected as a spray. Beach sand is typically added to form the combustion bed; if ash is generated, the ash can form the bed. No auxiliary fuel is required for liquid wastes with a heating value of at least 2900 Btu/lb. Utility requirements for a full-scale facility are 250 kW of electricity (Diot 1989; personal communication from R. Haney, Ogden Environmental Services, 1989).

Waste Generation

Thermal treatment technologies typically generate solid, liquid, and gaseous wastes that require additional treatment before their release or disposal. In comparison, liquid wastes are not generated during CBC operation, and air emissions are substantially reduced. Limestone can be added to the combustion loop to capture acid gases (SO_2 forms calcium sulfate or gypsum, and chloride forms calcium chloride). This eliminates the need for wet scrubbers, which would generate dilute aqueous acidic wastes. Water is only used in the CBC process for noncontact cooling. Therefore, no liquid wastes are generated.

With the elimination of sulfuric and hydrochloric acids, the only air pollutant emitted is NO_x . Because of the high destruction efficiencies in the combustion loop, only 30 to 40 percent excess air is required. This results in limited NO_x emissions.

Solid wastes are generated in the form of ash, which is periodically removed from the combustion loop, and fly ash, which is removed from the off-gases by a fabric filter system.*

* Personal communication from R. Haney, Ogden Environmental Services, 1989.

Demonstrated Waste Treatment

Ogden Environmental currently operates two full-scale transportable CBC systems. These units require 3 to 4 weeks for setup, are 30 ft by 50 ft at the base and 60 ft tall, require a work area 100 ft by 100 ft, and operate at rates of 100 to 150 tons/day. The first unit is incinerating PCB-contaminated soils in Alaska and is licensed under the Toxic Substances Control Act for treating PCB-contaminated wastes nationwide. The Alaska unit achieves 99.9999 percent destruction and removal efficiency (DRE) and a combustion efficiency of 99.9 percent; the PCB content of the treated soil is less than 0.2 ppm (Diot 1989). In PCB trial burns, NO_x emissions were less than 75 ppm (Jensen and Young 1986). The second CBC unit is treating fuel-contaminated soils at a site in California. At operating temperatures of approximately 900°C, less than 60 ppm NO_x is generated. Construction of two additional CBC units was expected to be completed during the winter of 1989.*

Both bench- and pilot-scale testing by Ogden Environmental have been performed on liquids, sludges, and solids containing diverse organic contaminants. Destruction efficiencies for several compounds have included 99.9999 percent for malathion in a liquid waste, 99.999 percent for dichlorobenzene in a sludge, and 99.9999 percent for "aromatic nitrile" as a tacky solid (Jensen and Young 1986).

A pilot-scale facility in San Diego, California, is available for use. This 16-in.-diameter facility is operated at a feed rate of 20 tons/day for solids or approximately 600 lb/h for liquids (1.2 gal/min). Approximate costs for a pilot-scale test could range from \$60,000 to \$250,000, depending on the exact nature of the waste and the analytical requirements.*

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

The CBC technology has not been tested with red water; however, results from pilot- and full-scale operations suggest that the theoretical potential for treatment is high.

* Personal communication from R. Haney, Ogden Environmental Services, 1989.

Current Application and Status of Technology

The CBC process has been fully demonstrated in pilot-scale studies on liquids that are not very similar to red water, and full-scale processes are in use for the treatment of solids.

Environmental Impact

No wastewaters are generated during CBC operations. The only significant air pollutant generated during treatment is NO_x , and it is typically generated at lesser rates than those of the more traditional thermal treatment technologies because of the reduced excess air conditions in the CBC process. Solid wastes are generated in the form of ash, which is periodically removed from the combustion loop, and fly ash, which is removed from the off-gases by a fabric filter system. Whether the chemical and physical characteristics of these solid wastes will differ from those in the ash generated during past incineration of Radford AAP red water is not known. Recycling of red water components is not feasible with the CBC process.

Time and Cost for Implementation

A pilot-scale study to determine red water treatment efficiencies and ash characteristics could be easily performed at the San Diego CBC facility. The study could be completed and full-scale operating parameters or the CBC design could be determined in less than 1 year. Costs for the pilot-scale test could range from \$60,000 to \$250,000, depending on the exact nature of the test and the analytical requirements.

Complexity, Operation, and Flexibility

The CBC process is not especially complex, and operation should not be difficult. Operating parameters appear to be rather flexible.

Evaluation Summary

Overall, the CBC technology appears favorable for red water treatment; however the characteristics of the ash that would be generated represent is a major data gap. Table D-14 presents a quantitative evaluation of the CBC technology based on five categories of evaluation criteria. The final score for the CBC process is 69 of a possible 110 points.

TABLE D-14. QUANTITATIVE EVALUATION OF CIRCULATING BED COMBUSTION

	<u>Points awarded</u>	
1. Theoretical potential for red water treatment		9
2. Current application and status of technology		13
3. Environmental impact		29
Wastewater discharge regulations	10	
Air emission regulations	7	
Solid/hazardous waste regulations	12	
Recyclability	0	
4. Time and cost for implementation		5
Time	3	
Cost	2	
5. Complexity, operation, and flexibility		13
Process complexity	3	
Difficulty of operation	3	
Flexibility of operating parameters	3	
Miscellaneous	4	
TOTAL		69

SONOCO SULFITE RECOVERY PROCESS (SSRP)

TECHNOLOGY DISCUSSION

Background

Over the last decade, the Sonoco Sulfite Recovery Process (SSRP) has been the most frequently recommended and the most thoroughly investigated technology for the treatment of red water generated from the production/purification of TNT. This technology was developed by the Sonoco Products Company in Hartsville, South Carolina, when environmental regulations promulgated in 1972 no longer allowed the discharge of black liquor (spent paper pulp cooking liquor) into streams.

Sonoco has been a producer of neutral sulfite semichemical (NSSC) pulp from local hardwoods since 1933. The SSRP was developed to recover sodium values from neutral sulfite semichemical paper pulp processing liquor. In neutral sulfite semichemical pulping, wood chips are cooked in a neutral solution of sodium sulfite (Na_2SO_3) and sodium bicarbonate (Na_2HCO_3). The spent solution contains dissolved lignin from the wood. This solution is first concentrated to 55 to 60 percent solids and then sprayed into a furnace. The solution has sufficient fuel value to evaporate the remaining water, to support combustion, and to supply steam and power for the mill. The sodium values are recovered as a molten smelt that contains sodium sulfide and sodium carbonate. This smelt may be processed further to produce Na_2SO_3 and NaHCO_3 for recycle.

In the Sonoco Process, hydrated alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is added to the liquor after the wood cooking and prior to treatment in the furnace. Sodium values are converted to water-soluble sodium aluminate (NaAlO_2), and sulfur compounds are oxidized from hydrogen sulfide (H_2S) to sulfur dioxide (SO_2). The sodium aluminate solution absorbs sulfur dioxide in a gas scrubber, which produces sodium sulfite and hydrated alumina for recycle. An advantage of the Sonoco Process is that sodium aluminate remains solid in the furnace, whereas sodium sulfide and sodium carbonate form slags that set up and are hard to handle.

The Sonoco Process would have to be modified to treat red water. Red water and spent wood pulping solution are similar in that both contain dissolved organic matter and soluble sodium salts, which are potentially recyclable; however, the following significant differences also exist:

- ° The organic matter in paper pulp liquor is a water-soluble lignin sulfite that has sufficient fuel value both to reduce inorganic sulfur compounds to sulfides and to provide steam and power for the plant. The organic matter in red water consist primarily of sodium salts of dinitrotoluene sulfonates. The fuel value of red water solids is barely sufficient to sustain combustion on a dry solids basis (about 3200 Btu/lb). Hence, red water reduction would require an energy input.
- ° Red water contains significant quantities of sodium nitrate (NaNO_3) and sodium nitrite (NaNO_2). Sodium nitrate decomposes at 380°C ,³ and sodium nitrite decomposes at 320°C (Weast 1980). In the furnace, these compounds will probably decompose to sodium oxide (Na_2O) and nitrogen oxides (NO_x).
- ° In paper pulp liquor, organic matter (reducing agent) and sodium salts (reductant) are both in solution; therefore, mixing is much more intimate than can be achieved by mechanical means such as grinding. Excellent blending of fuel and organic matter results. In the decomposing of red water, supplemental fuel (probably petroleum coke) will be needed, and the chemical reaction rates will be controlled by contact between different phases: gas-solid, liquid-solid, and solid-solid. Fuel usage and requirements will vary.

Development of the Sonoco Process as It Applies to Red Water

The U.S. Army has spent considerable time, money, and effort in developing the SSRP for red water treatment. This effort has been seriously limited because no RAAP red water is available for testing and evaluating of equipment. Table D-15 presents a summary of the process stages of the SSRP and the level of testing to date with red water or other wastes.

The reduction section of the Herreschoff-type furnace has received limited pilot-plant testing. Calcined petroleum coke has also received limited pilot-plant testing as the furnace fuel (Eckenrode, Denzler, and Klein 1980; Helbert, Pregun, and Carrazza 1983). Low sulfur, calcined petroleum coke is very much in demand as an electrode material, however, and commands a price of about \$500 per ton.* "Green" or uncalcined petroleum coke would probably be a more economical fuel, even if the efficiency were

TABLE D-15. RAAP SULFITE RECOVERY SYSTEM:
LEVEL OF TESTING OF MAJOR SECTIONS OF THE SYSTEM^a

- A. Tested on a pilot-plant scale with red water from another Army ammunition plant:
 - 1. Herreschoff-type furnace--reduction section only, batch operation, five tests showed up to 86 percent conversion.
 - 2. Petroleum coke as a reducing agent--batch operation, four tests.
- B. Tested on a pilot-plant scale with materials other than red water:
 - 1. SO₂ absorber--batch operation with no aluminum compounds or suspended solids present.
 - 2. Centrifuge for solids separation--synthetic suspensions and Sonoco furnace ash from a paper mill.
- C. Tested on a laboratory scale with materials originating with red water from another Army ammunition plant:
 - 1. TNT purification with regenerated sellite--batch tests with the sellite having been through one cycle only.
- D. Tested on a laboratory scale with materials other than red water:
 - 1. Multiple-hearth furnace gas streams afterburner--synthetic mixtures only.
- E. No testing, assumed will work by analogy with similar equipment at another Army ammunition plant:
 - 1. Multiple-effect red water evaporation.
- F. No testing, assumed will work by analogy with similar equipment at paper mills using the Sonoco Process:
 - 1. Ash-handling system

TABLE D-15 (continued)

F. (continued)

2. Ash-dissolving system
3. Particulate-control system--cyclone, wet dust collector, particulate scrubber
4. Waste-heat boiler

G. No testing

1. Herreschoff furnace--oxidation section
 2. Red water condensate recovery system--hollow-shaft evaporator and condensers.
 3. Integrated system under continuous operation with sellite recycle to the TNT plant for a protracted period of time.
 4. Requisite aluminum-to-sodium ratio
 5. Electrostatic precipitator
 6. Instrumentation and control system
-

^a Summarized from Eckenrode, Denzler and Klein 1980; Helbert, Pregun, and Carrazza 1983; Helbert and Stull 1984; and Foster Wheeler 1988.

lower. Sulfur and metals present in crude oil preferentially report to petroleum coke in the refinery. A typical petroleum coke will contain 1.5 to 10.0 percent sulfur and 0.1 to 2.8 percent ash (Perry and Green 1984). The sodium oxide produced by the decomposition of sodium nitrate and nitrite may be able to absorb the sulfur from the coke. Sodium oxide may also accumulate on reactor walls or leach silica and alumina from refractory brick.

The SO_2 absorber and centrifuge have been tested on a pilot-plant scale with synthetic mixtures (Helbert, Pregun, and Carrazza 1983; Helbert and Stull 1984). The process gas streams will be hot, will contain suspended particulate matter, and will probably fluctuate in temperature and composition. The aluminum-to-sodium ratio required for the process will have an impact on the quantity of suspended solids fed to the centrifuge and, hence, on centrifuge loading. The filterability of the actual process stream has not been addressed.

Purification of TNT with regenerated sellite has been tested on a laboratory scale with sellite that has been through one regeneration cycle only (Helbert, Pregun, and Carrazza 1983). In an operating plant, the sellite will have been through multiple regeneration cycles. Buildup of impurities such as metals, silica, and products resulting from the incomplete destruction of red water solids may affect the sellite's performance and the quality of the purified TNT.

The multiple-hearth-furnace gas stream afterburner has been tested with synthetic mixtures on a laboratory scale (Eckenrode, Denzler, and Klein 1980; Helbert, Pregun, and Carrazza 1983). Problems associated with scale-up, suspended solids, and fluctuating feed conditions have not been addressed.

The multiple-effect red water evaporator design is adopted from that of a similar unit at another Army ammunition plant. A typical evaluation procedure would involve test runs of RAAP red water in the proposed evaporator. Unanticipated problems may result.

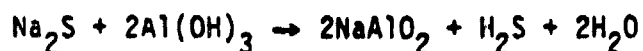
* Personal communication from M. Poultry, Airco Carbon, Port Lavaca; S. Foster, Airco Carbon, Pittsburgh, Pennsylvania; D. Laird, Great Lakes Carbon Co., Port Arthur, Texas; and F. Louis, AMOCO, Chicago, Illinois, March 30, 1989.

The ash-handling system, the ash-dissolving system, the particulate control system (cyclones, wet dust collector, particulate scrubber), and the waste-heat boiler have not been tested. Similar equipment has worked successfully in a paper mill, and it is assumed that technology transfer to a TNT plant will present no serious problems. The Foster Wheeler report (1988) pointed out areas where potential problems may exist. These are summarized in Table D-16.

Finally, several systems for which operating conditions will be substantially different for red water than for wood pulp have not been tested. These include 1) the oxidation section of the multiple-hearth furnace, 2) the use of one multiple-hearth furnace for both oxidation and reduction, 3) the red water condensate recovery system, 4) the electrostatic precipitator, 5) the requisite aluminum-to-sodium ratio, and 6) the integrated system and the effects of cyclic operation. The plant instrumentation and control system is strictly a paper design.

Figure D-10 presents a simplified process schematic of the SSRP as it would be applied to red water. The process and proposed modifications have been described in detail in previous reports (Eckenrode, Denzler, and Klein 1980; Helbert, Pregun, and Carrazza 1983; Helbert and Stull 1984). Table D-17 represents the material balance. Development of this material balance was based on the 1980 CSL Report (Eckenrode, Denzler, and Klein) and is used to assess the impact of varying process parameters that have not been fully established. This mass balance was prepared to reflect the process under the most favorable conditions.

The material balance presented in Table D-17 shows aluminum and sodium at the atomic ratio of 1 to 1, or the stoichiometric ratio, as did the material balance presented in the 1980 CSL Report:



In practice, however, an excess of aluminum would be used to force a more complete conversion of sodium values to soluble sodium aluminate (NaAlO_2). The Sonoco paper mill used an aluminum-to-sodium atomic ratio of about 1.2 to 12. The furnace test results using petroleum coke show aluminum-to-sodium ratios of 2.3 to 3.2, and some laboratory work was done at a 5 to 1 ratio

TABLE D-16. SUMMARY OF POTENTIAL PROBLEMS OF SSRP
FOR TREATMENT OF RED WATER^a

A. Recommended Testing Program:

1. Vendor tests of the multiple hearth furnace in the combined reducing and oxidizing mode.
2. Vendor tests of the hollow-shaft evaporator.
3. Vendor tests of the SO₂ absorber and particulate scrubber.
4. Vendor tests of the electrostatic precipitator.
5. Centrifuge tests to verify solids removal efficiency and to identify any scaling problems.
6. Tests of the ash cooler.

B. Engineering Assessments of Major Process Components:

1. Multiple-effect evaporator--The unit at Volunteer Army Ammunition Plant has four stages. The proposed unit has three stages. Foster Wheeler recommended the four-stage unit with a condenser on the third stage.
2. Hollow-shaft evaporator--The proposed size is adequate if the Mason and Hanger (M&H) material balance is correct. Extra solids may result from an increased aluminum-to-sodium atomic ratio, which could overtax the evaporator.
3. Multiple-hearth furnace--The design was based on one pilot test. Unresolved issues are excessive sodium losses, lower-than-projected furnace efficiency, aluminum-to-sodium ratio, carbon utilization lower than the design rate (42 vs. 100 percent), conversion of the unreacted H₂S to Na₂SO₄ (design assumed the seventh and eighth furnace compartments), and pilot testing of the furnace in the oxidizing mode.
4. Electrostatic precipitator--No experimental surface-to-volume sizing data are available. Volatile sodium compounds could cause sticking and caking on the ESP collector surface. Unevaporated quench water spray could also cause caking on the ESP collector surface.
5. Afterburner--The M&H design showed 0.03 percent oxygen (v/v) in the exit gas. Foster Wheeler (1988) recommended 4 percent oxygen (v/v). The increased oxygen content in the exit gas would ensure complete combustion of H₂S to SO₂; however, this would increase

TABLE D-16 (continued)

the exit volume because of the extra oxygen and accompanying nitrogen. As a result, a larger afterburner, waste-heat boiler, and other downstream equipment would be required.

6. Waste-heat boiler--Foster Wheeler recommended a fire tube unit with sprays before the mist eliminator for intermediate washing.
 7. SO_2 adsorber and particulate scrubber--Foster Wheeler recommended clip-on trays rather than welded trays. Additional trays may be required because 4 percent oxygen would increase the gas flow rate.
 8. Centrifuge--Foster Wheeler noted that the solids removal efficiency was 55 to 76 percent rather than the 98 percent projected by the vendor. The M&H material balance indicated a normal flow rate of 55.3 gal/min. The bid specification showed 50 gal/min. The solids content in the centrifuge feed was 26.6 percent in the M&H material balance and 11.8 percent in the bid specification. Foster Wheeler recommended a design feed rate of 30 percent above normal and an increase in solids content to 45 percent to allow for unresolved process parameters.
 9. Ash cooler--Foster Wheeler indicated concern about the difference in heat flux between pilot tests, design specifications, and M&H design specifications, which were 760, 4200, and 6614 Btu per square foot, respectively. Foster Wheeler also recommended additional tests.
- C. Other Engineering Assessments Indicating Potential Difficulties:
1. The nitrogen gas system may be undersized.
 2. Sixteen or more pumps may be subject to excess erosion and/or corrosion.
 3. The red water slurry transfer system may not supply slurry fast enough.
 4. Foster Wheeler recommended a redesign of the hollow shaft evaporator feed system.
 5. The boiler feed water treatment and supply system should be upgraded.

^a Source: Foster Wheeler 1988.

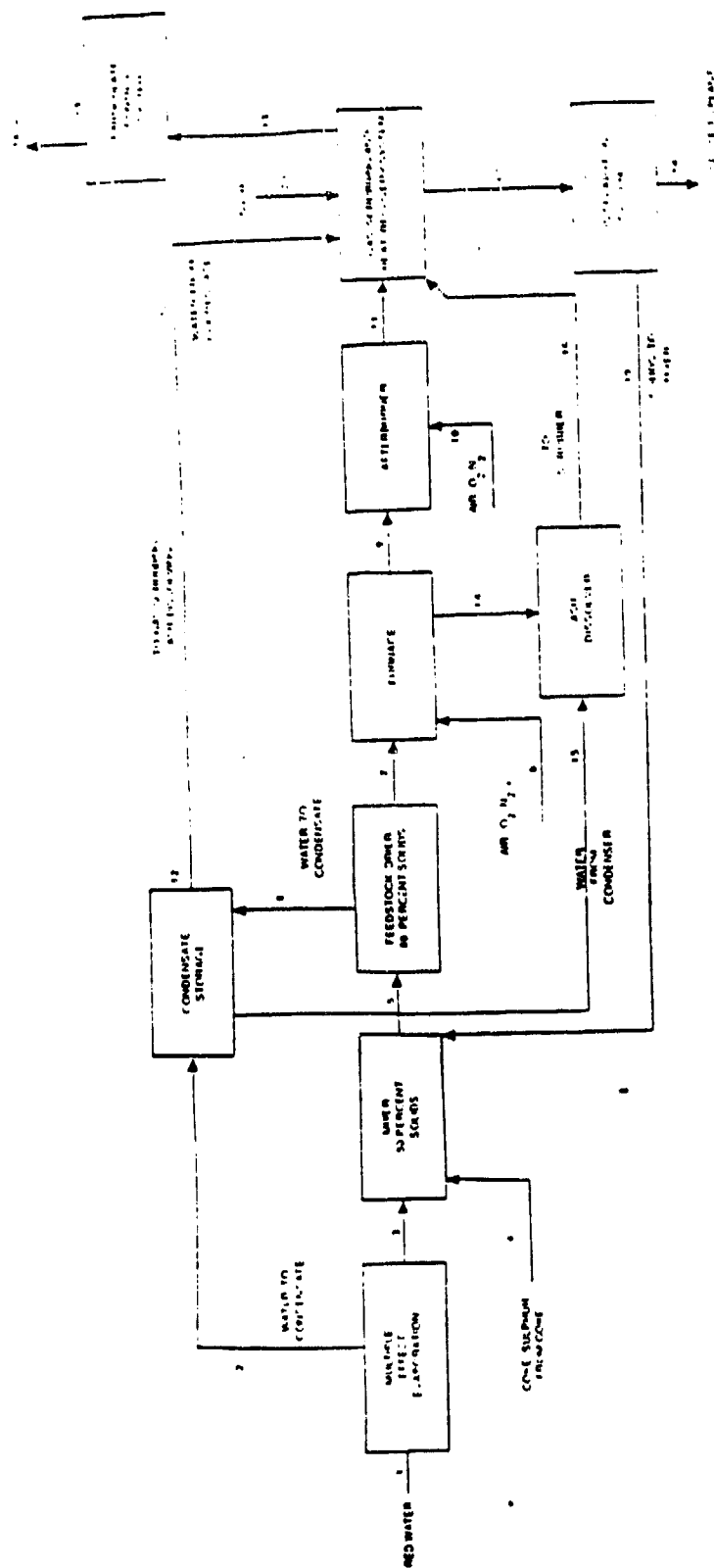


Figure D-10. Process Schematic of the Sonoco Process for treatment of RAAP red water.

Source: Eckenrode, Denzler, and Klein 1980.

TABLE D-17. MATERIAL BALANCE FOR TREATING RAAP RED WATER USING THE SONOCO PROCESS^a
(lb/h)

Stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Total mass	6416	3667	2749	156	3689	1438	2251	2924	4499	1033	5532	730	6713	676	4375	5051	4623	3839	794	20
Water	5454	3667	1787	0	1888	1438	450	0	687	0	768	730	2266	0	4375	4375	3387	3281	101	0
Soluble solids	962	0	962	0	975	0	975	0	27	0	0	0	0	631	0	631	571	558	13	20
Insoluble solids	0	0	0	156	826	0	826	0	0	0	0	0	0	45	0	45	670	0	670	0
Gases other than water	0	0	0	0	0	0	0	2924	4247	1033	4737	0	4447	0	0	0	0	0	0	0
Na ₂ SO ₃	246	0	246	0	259	0	259	0	0	0	0	0	0	0	0	0	571	558	13	0
Na ₂ SO ₄	64	0	64	0	64	0	64	0	0	0	0	0	0	0	0	0	0	0	0	0
NaNO ₂	108	0	108	0	108	0	108	0	0	0	0	0	0	0	0	0	0	0	0	0
NaNO ₃	14	0	14	0	14	0	14	0	0	0	0	0	0	0	0	0	0	0	0	0
Sodium DMT sulfonate	353	0	353	0	353	0	353	0	0	0	0	0	0	0	0	0	0	0	0	0
Alpha-TMT-sellite	177	0	177	0	177	0	177	0	0	0	0	0	0	0	0	0	0	0	0	0
Na ₂ O	0	0	0	0	0	0	0	0	27	0	27	0	0	0	0	0	0	0	0	0
NaOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	20
NaAlO ₂	0	0	0	0	0	0	0	0	0	0	0	0	0	631	0	631	0	0	0	0
Al(OH) ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	670	0	670	0
Al ₂ O ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	45	0	45	0	0	0	0
Carbon from coke	0	0	0	150	150	0	150	0	0	0	0	0	0	0	0	0	0	0	0	0
Sulfur from coke	0	0	0	6	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	290	0	0	0	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0	0	0	154	0	0	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0	0	1115	0	1115	0	1115	0	0	0	0	0	0	0

(continued)

TABLE D-17 (continued)

Stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
NO _x	0	0	0	0	0	0	0	0	206	0	206	0	206	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	0	0	614	0	217	0	0	0	0	0	0	0	0	0	0
N ₂	0	0	0	0	0	0	0	2310	2310	816	3126	0	3126	0	0	0	0	0	0	0

^a Source: Derived from Eckenrode, Denzler, and Klein 1980.

ASSUMPTIONS

- Analyses of RAAP red water are as presented in "Review of Canadian Industries Limited's Bolocel Facility as a Candidate Site for a SRP Pilot Test." Radford Army Ammunition Plant, October 26, 1988.
- Relative proportions of sodium sulfate and sodium sulfite are as presented in Carrazza et al. (1984).
- Red water organics are assumed to be solely isomeric sodium dinitrotoluene sulfonates (2/3 of organics) and the alpha-TNT-sulfite complex (1/3 of organics).
- Chemical nitrogen compounds are converted to nitrogen in the furnace and are converted to NO_{1.5} in the afterburner. Atmospheric nitrogen remains as such.
- Atomic weights used are whole numbers; Na = 23, H = 1, C = 12, O = 16, S = 32, N = 14.
- Sodium nitrate and sodium nitrite decompose in the reduction furnace to Na₂O and N₂. The N₂ is oxidized to NO_{1.5} in the afterburner.
- The coke contains 4% sulfur and is ashless.
- Metals other than sodium in red water are not considered.
- Only the oxygen (in air) used to burn H₂S to SO₂ in the afterburner is considered.
- The temperature drop across the hot gas scrubber is 500°F.
- The product is a 14.5% sellite solution (Stream 18). This is assumed to be satisfactory. If a 15% sellite solution is required for TNT production, there would be a condensate accumulation.
- No reactions take place in the oxidizing section of the furnace.

(Eckenrode, Denzler, and Klein 1980). The excess aluminum will be carried through the process as water-insoluble solids, either as aluminum hydroxide $[\text{Al}(\text{OH})_3]$ or aluminum oxide (Al_2O_3).

The material balance in Table D-17 indicates 27 pounds per hour of sodium oxide (Na_2O) being volatilized and not reacting with aluminum (Streams 9 and 11). The Na_2O is captured in the gas-scrubbing system and reacts with sulfur dioxide to form sodium sulfite (sellite). Streams 14 and 16 are small amounts of aluminum oxide that are converted to aluminum hydroxide and recycled; however, all excess aluminum is converted to water-insoluble $\text{Al}(\text{OH})_3$ and would greatly increase the quantities of water-insolubles in the process. The water-insolubles could interfere with the use of this slurry for SO_2 scrubbing.

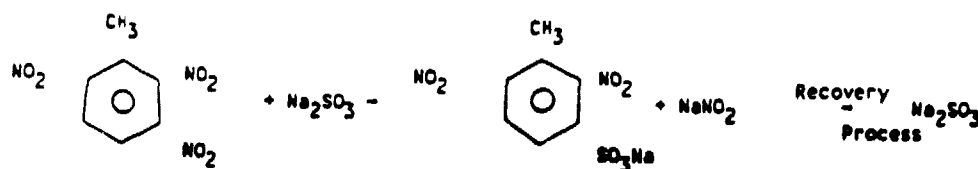
An undefined required excess of aluminum has an impact on several process streams and will also have an impact on the required size of the equipment used to process and convey water-insoluble solids:

- ° The mass fed to the feed stock dryer (Stream 19) is primarily $\text{Al}(\text{OH})_3$ as an 85 percent insoluble solids cake. Doubling the aluminum-to-sodium ratio would double the quantity of insoluble solids going into the dewatering system and conveyed from the system to the mixer.
- ° The mixer produces an approximately 50 percent solids blend of red water, $\text{Al}(\text{OH})_3$, and petroleum coke. Because a pound of $\text{Al}(\text{OH})_3$ will require a pound of water, increasing the $\text{Al}(\text{OH})_3$ fed to the dryer will reduce the amount of water evaporated in the multiple-effect evaporator (Stream 2) and increase the amount of water evaporated in the feedstock dryer (Stream 6). Fixing the ratio would allow an economic sizing of the production-scale multiple-effect evaporator, mixer, feedstock dryer, and solids-conveying systems.
- ° The excess $\text{Al}(\text{OH})_3$ will be converted to Al_2O_3 in the furnace. This will affect the heat loading to the furnace by increasing the quantity of water that is evaporated from the furnace and $\text{Al}(\text{OH})_3$ that is converted to Al_2O_3 . An increased quantity of solids will have to be processed through the eight compartments of the furnace.
- ° Although the material balance does not show suspected solids in the furnace exit gas (Stream 9), adding additional $\text{Al}(\text{OH})_3$ will increase the quantity of suspended solids that will be captured in the particulate control system (Stream 13) and will influence the choice of electrostatic precipitators. Some of the excess solids may be removed in the scrubber.

- ° The insoluble solids reporting to the ash dissolver (Stream 14) could be as low as 45 pounds per hour at a 1 to 1 atomic ratio of aluminum-to-sodium or as high as 2726 pounds per hour at a 5 to 1 atomic ratio. At the stoichiometric ratio, most of the aluminum present is converted to water-soluble NaAlO_2 . In the ash dissolver, Al_2O_3 is converted to an $\text{Al}(\text{OH})_3$ suspension. In the latter case, the suspension sent to the scrubber (Stream 16) could be as high as 34 percent solids. At that high level of suspension, the liquid might not be suitable for SO_2 scrubbing. This could be resolved by filtering part of the slurry stream after the ash dissolver and before the gas scrubber. The choice of type and size of the additional filtering system could be improved by laboratory or pilot-plant testing.
- ° The washed filter cake (Stream 19) will be about 85 percent $\text{Al}(\text{OH})_3$ and 15 percent sellite solution.* Additional aluminum in the system would increase the quantity of sellite recycled to the furnace rather than returned to the plant. As long as an 85 percent solids $\text{Al}(\text{OH})_3$ filter cake can be obtained, this should not be a problem. If the filter cake has a significantly lower solids content, however, the impact could be very serious and result in both reduced sellite recovery and increased amounts of material reprocessed throughout the system.

An advantage of the Sonoco Process is that a hazardous waste stream is converted into a product that can be reused on site. Although the production cost of sellite at this facility will most likely be greater than the purchase price of sellite, the difference will be offset by the elimination or reduction of disposal of a RCRA hazardous waste.

The material balances shown in Table D-17 and in the 1980 CSL Report show no process effluent. In both cases, this is an oversimplification. Red water processing could produce more sellite than is required for TNT purification as a result of the red water containing process wastes other than those resulting from TNT purification. The TNT purification reaction is:



* Personal communication from W. Lew, Reynolds Aluminum Co., Gregory, Texas, April 5, 1989.

The reactants and products each contain two sodiums and one sulfur. If recovery of sellite from the dinitrotoluene sulfonates and sodium nitrite is 100 percent, the sellite generated in the Sonoco Process would just equal the sellite consumed in TNT purification. In the TNT plant, however, additional sodium (as sodium nitrate and sodium sulfate) is introduced into the red water to neutralize the nitric and sulfuric acids. The sodium sulfate also introduces additional sulfur. Petroleum coke also contains sulfur; in the Sonoco Process, this would be converted to sellite. (Table D-17 shows that the cake contains 4 percent sulfur and introduces 6 pounds of sulfur per hour.

Any surplus sellite would be present as an approximately 15 percent aqueous solution. This solution could be used in a paper mill that used sulfite pulping; however, making the sellite marketable may require evaporating part or all of the water and entail absorbing part or all of the transportation cost. The advantage of using SSRP at RRAP is that the residue from the treatment of a hazardous waste would be converted to a marketable product.

Use of this process also has some disadvantages. Metal-containing ash from red water and petroleum coke will build up in the plant as insoluble aluminum compounds. Red water will contribute about 104 lb/day of iron, magnesium, chromium, copper, and cadmium. Coke ash (0.1 to 2.8 percent of the petroleum coke) will contribute about 36 lb/day of vanadium and other metals (at 1 percent ash). Silica may be leached from the furnace refractory by volatile sodium compounds. Separation processes would have to be developed. Aluminum might be separated from the metal oxides by dissolving it in alkali; this would leave residues of metal oxides that would have to be disposed of. Red water metals may be in solution as organic salts, but the organic compounds will be decomposed in the furnace and the metal oxides will be precipitated in the alkaline scrub solution.

Startup of a red water treatment plant may be difficult. Although the Sonoco process has been used successfully in the pulping industry, the high temperature operations (1750°F), corrosive gases (NO_x , Na_2O , SO_2 , and H_2S), and abrasive solids (alumina) require efficient separation of the solids from gases and from the liquids. No process development work has been done with

RAAP red water. Sonoco Products Company shut down their unit about 4 or 5 years ago, and none of the technical people who worked on the process are still at Sonoco.* Smorgon Consolidated Industries PTY, Ltd., of Melbourne, Australia, also shut down their plant when they changed their wood pulping technology. Sonoco has licensed the technology only to the Australians and the U.S. Government, and no facility currently uses the Sonoco Process in a commercial-scale operation. Consequently, no technical assistance from personnel with process operating experience is likely to be available. Such assistance would be very useful.

A facility that uses a new technology or an existing technology in a new application can expect to encounter some problems during startup; e.g., equipment may not be suitable for the intended purpose, improper construction materials may have been chosen, and equipment capacities may be less than expected. Treatment of red water with the Sonoco Process will be no exception.

An additional complication, regardless of the selected red water treatment process, is that the treatment facility and the TNT plant would be started up simultaneously. Although TNT production is a proven and established technology, the startup of a plant that has been mothballed for several years usually presents some problems. Resolving these problems will place demands on the technical and managerial staff at the same time they are faced with startup of the red water treatment facility. If possible, startup of a red water treatment facility should be deferred until the TNT plant is operational.

An integrated process (or even simultaneous testing of two process components) has not been tested; however, full-scale SSRP plants for treatment of black liquor have operated successfully.

TECHNOLOGY EVALUATION

Theoretical Potential for Red Water Treatment

Laboratory analysis indicates that the constituents of red water are similar to those of black liquor, which has been successfully treated in the

* Personal communication from M. Cunningham, Sonoco Products Company, Hartsville, South Carolina, April 5, 1989.

SSRP with satisfactory sellite recovery and environmental controls. Numerous laboratory and pilot-scale tests have been performed on the individual equipment components of the SSRP treatment train for red water; again, results were satisfactory or promising. Other equipment components that have not been demonstrated are nearly identical in design and operation to units now being used for other purposes at other AAPs. Theoretically, the treatment of red water by the SSRP appears technically feasible.

Current Application and Status of Technology

The SSRP has been installed for black liquor treatment and has performed successfully at two of three installations worldwide. The unsuccessful use of the SSRP at Groveton Paper Company, Groveton, New Hampshire, was attributed to "poor engineering." Because the SSRP at Sonoco Products Co. in Hartsville, South Carolina, and the one at Smorgon Consolidated Industries PTY, Ltd., in Melbourne, Australia, have been shut down, it may be difficult to find experienced personnel. The technology has been proven at full scale on a waste stream similar to red water, however, and considerable laboratory and pilot tests on individual equipment components have been performed to evaluate their effectiveness for red water treatment. Also, a full-scale SSRP has been designed for RAAP. Construction of the facility was initiated in June 1985 and terminated 3 years later because of numerous change orders. Of all the treatment technologies currently available, the SSRP has been evaluated the most thoroughly.

An integrated process (or even simultaneous testing of two process components) has not been tested; however, full-scale plants for treatment of black liquor have been operated successfully.

Environmental Impact

Wastewater Discharge Regulations--

Laboratory investigations have produced a filtrate that can be reused in the TNT production plant. Unfortunately, these investigations were not thorough enough to determine whether continuous recycling of the products would lead to a buildup of impurities that could ultimately affect TNT specifications.

Air Emissions--

Laboratory investigations have provided a basis for sizing the SO₂ scrubber. The particulate matter loading depends greatly on the aluminum-to-sodium ratio and the ash content of the carbon reducing agent, neither of which has been defined. This loading will have an impact on the size of the particulate control system. Although the proposed particulate control system is a proven technology, the aluminum-to-sodium ratio must be defined before the equipment can be properly sized.

Complexity, Operation, and Flexibility

Process Complexity--

The furnace operates at 1750°F and involves a novel scheme of separate zones to produce both reduced and oxidized output. Both liquid and gaseous process streams contain suspended abrasive solids that require clean separation. Impurities also may build up in material that is recycled. Many of these complexities are not yet resolved.

Difficulty of Operation--

Use of the SSRP for red water treatment is expected to be difficult because of the simultaneous operation of a single furnace in an oxidizing and reducing mode, the large-scale processing of potentially explosive organic nitro compounds, and the numerous operations requiring phase separations.

Flexibility of Operating Parameters--

The ranges of required aluminum-to-sodium ratios must be firmly defined. Deviation from these established parameters may lead to incomplete treatment. The SSRP is not expected to have large turndown capabilities because this would greatly reduce treatment efficiencies.

Miscellaneous--

The Sonoco Process is not currently in operation anywhere, not even in paper mills. Those persons who built and started up the Sonoco Products plant in Hartsville, South Carolina, are no longer with Sonoco; thus, technical assistance may be unobtainable.

Evaluation Summary

Table D-18 presents a qualitative evaluation of the Sonoco Sulfite Recovery Process based on five categories of evaluation criteria. The final score for the SSRP is 63 of a possible 110 points.

TABLE D-18. QUANTITATIVE EVALUATION OF THE SONOCO SULFITE RECOVERY PROCESS

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	9
2. Current application and status of technology	14
3. Environmental impact	33
Wastewater discharge regulations	5
Air emission regulations	5
Solid/hazardous waste regulations	15
Recyclability	8
4. Time and cost for implementation	3
Time	2
Cost	1
5. Complexity, operation, and flexibility	4
Process complexity	1
Difficulty of operation	1
Flexibility of operating parameters	1
Miscellaneous	1
TOTAL	63

REFERENCES FOR APPENDIX D

- Andrews, C. C. 1980. Photooxidative Treatment of TNT Contaminated Wastewaters. In: Chemical Abstracts 94:162133p.
- Basta, N. 1986. Use Electrodialytic Membranes for Waste Recovery. Chemical Engineering, March 3.
- Burrows, W. D. 1983. Tertiary Treatment of Effluent from Holston Army Ammunition Plant Industrial Liquid Waste Treatment Facility. 3. Ultraviolet Radiation and Ozone Studies: TNT, RDX, HMX, TAX, and SEX. Cited in Chemical Abstracts, 101:97063n.
- Carrazza, J., et al. 1984. Treatment of Wastewater (Red Water) Resulting from TNT Purification. Paper AD-P004-146. In: Proceedings of the 13th Environmental Systems Symposium, Bethesda, Maryland, March 20-22.
- Chemical Engineering. 1989. Chemical Engineering Plant Cost Index.
- Chemical Marketing Reporter. 1989. Chemical Prices. February 6.
- DeCicco, S., and W. Troxler. Undated. Mobile Thermal Treatment Systems. International Technology Corporation.
- Diesen, R., and J. Moyer. 1976. Wet Combustion of Organics. United States Patent No. 3,984,311.
- Diot, H. 1989. Update on the Use of Circulating Bed Combustion for Site Remediation. Presented at the APCA Annual Meeting and Exhibition, June.
- Eckenrode, J., G. Denzler, and J. Klein. 1980. Evaluation of TNT Red Water Pollution Abatement Technologies. Final Report. Environmental Technology Division, Chemical Systems Laboratory. Technical Report ARCSL-TR-80023.
- Fochtman, E. G., and J. E. Hoff. 1975. Ozone-Ultraviolet Light Treatment of TNT Wastewaters. In: Proceedings of the Second International Symposium on Ozone Technology, Montreal, Canada, May 11-14, 1975.
- Foster Wheeler. 1988. Investigation into the Status of Possible Alternatives for Disposal and/or Reuse of TNT Red Water.
- Foster Wheeler USA Corporation. 1988. Final Report on Treatment of TNT Thick Liquor. FW Reference No. 1-15-01-37.
- Fox, R. 1988. Memorandum on Alternative Technologies for Red Water Treatment. International Technology Corporation, Knoxville, Tennessee.

- Freeman, D. 1984. Continuous Fixation and Removal of Explosive Wastes from Pink Water Using Surfactant Technology. In: Proceedings of the 39th Industrial Waste Conference, Purdue University, West Lafayette, Indiana.
- Helbert, Jr., W., E. Pregun, and J.A. Carrazza. 1983. Recovery of Sellite from TNT Red Water. U.S. Army Armament Research and Development Command, Dover, New Jersey. Contractor Report ARLCD-CR-82010.
- Helbert, Jr., W., and H. Stull. 1984. Red Water Pollution Abatement System. U.S. Army Armament Research and Development Command, Dover, New Jersey. Contractor Report ARLCD-CR-83024.
- Helsel, R., et al. Undated. Technology Demonstration of a Thermal Desorption/UV Photolysis Process for Decontaminating Soils Containing Herbicide Orange.
- IT Envirosience. 1981. Evaluation of Catalyzed Wet Oxidation for Treating Army Lagoon Sediments. Knoxville, Tennessee.
- International Technology Corporation. Undated. Brochure: On-Site Treatment. Transportable Hybrid Thermal Treatment System. Knoxville, Tennessee.
- Jain, K. K. 1976. Laboratory Study on Feasibility of Munitions Wastewater Treatment by Adsorption-Oxidation. Prepared for the U.S. Army Mobility Equipment Research and Development Center under Contract No. DAAG3-75-C-0273.
- James W. Hudson and Associates. 1984. Treatment of TNT Thick Liquor Radford Army Ammunition Plant. Value Engineering Study and Workshop. Final Report. Prepared for Department of the Army, Norfolk District, Corps of Engineers. Project 60.
- Jensen, D., and D. Young. 1986. PCB-Contaminated Soil Treatment in a Transportable Circulating Bed Combustor. Presented at the Hazardous Materials Management Conference and Exposition, April-May.
- Kaplan, D., and A. Kaplan. 1982. 2,4,6-Trinitro-Surfactant Complexes: Decomposition, Mutagenicity, and Soil Leaching Studies. Environmental Science and Technology, 16(9):566.
- Miller, R., and M. Swientoniewski. 1981. The Destruction of Various Organic Pollutants by a Catalyzed Wet Oxidation Process. IT Envirosience, Knoxville, Tennessee.
- Nielson, R., and M. Cosmos. 1988. Low Temperature Thermal Treatment (LT³) of Volatile Organic Compounds from Soil: A Technology Demonstrated. Presented at the 1988 Summer National Meeting of the American Institute of Chemical Engineers.
- Noss, C.I., and H. Chyrek. 1984. Tertiary Treatment of Effluent from Holston Army Ammunition Plant Industrial Liquid Waste Treatment Facility. 4. Ultraviolet Radiation and Hydrogen Peroxide Studies: TNT, RDX, HMX, TAX, and SEX. Cited in Chemical Abstracts, 102-31420r.

- Okamoto, Y., et al. 1982. Removal of 2,4,6-Trinitrotoluene (TNT) and 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) from Aqueous Solutions with Surfactants. *Propellants, Explosives, Pyrotechnics*, 7:18.
- PEI Associates, Inc. 1989. Red Water Treatment Technology Evaluation. Project Initiation Meeting. Written Summary. January 19.
- Perry, R. H., and D. W. Green, eds. 1984. *Perry's Chemical Engineer's Handbook*. 6th ed. McGraw-Hill Book Company, New York.
- Peters, M., and K. Timmerhaus. 1980. *Plant Design and Economics for Chemical Engineers*. 3rd ed. McGraw-Hill Book Company, New York.
- Radford Army Ammunition Plant. 1988. Review of Canadian Industries Limited's Boloeil Facility as a Candidate for a SRP Pilot Test.
- Seidman, M. 1956. Oxidation of Liberty Powder TNT Red Waste Liquors. Internal Research Memorandum, Zimpro/Passavant Corporation, April 19.
- Semmens, M. J., D. Barnes, and M. O'Hara. 1985. Treatment of an RDX-TNT Waste from a Munitions Factory. In: *Proceedings of the 39th Industrial Waste Conference*, Purdue University, West Lafayette, Indiana.
- Sierka, R. A. 1985. The High Temperature Treatment of Trinitrotoluene (TNT) and Cyclotrimethylene-Trinitroamine (RDX) with Ozone and Ultrasound, Ozone. *Science and Engineering*, 6:275-290.
- T-Thermal. 1989. T-Thermal Waste Disposal and Recovery Systems Bulletin No. 150.487-5M.
- Weast, R., ed. 1980. *CRC Handbook of Chemistry and Physics*. 61st ed. CRC Press, Inc. Boca Raton, Florida.
- Westinghouse Environmental Services. 1988. Brochure: Thermal Destruction, Pyroplasm. July.
- Zimpro/Passavant Corporation. Updated. Wet Air Oxidation of Hazardous Waste.

APPENDIX E

EFFECTS OF SODIUM SALTS ON
HAZARDOUS WASTE INCINERATOR PERFORMANCE AND OPERATION

PEI ASSOCIATES, INC.

MEMORANDUM

TO: Project File

DATE: December 15, 1988

SUBJECT: Effects of Sodium Salts on
Hazardous Waste Incinerator
Performance and Operations

FROM: J. E. Spessard *JS*

FILE: PN 8747

cc: C. M. Harvey
T. C. Ponder, Jr.

Aqueous waste streams at Texas Eastman's Longview, Texas plant contain significant quantities of sodium salts (formate, acetate, carbonate, and chloride). I have contacted incinerator and refractory vendors to learn how this would affect incinerator and refractory performances and costs. Incinerating these sodium salts will require a more expensive refractory which will have a shorter service life. The refractory will be particularly susceptible to damage due to process upsets. The incinerator control systems, operator procedures, and maintenance effort will all require more attention than for a normal liquid incinerator. Capital costs will be about 20 percent higher than for incinerating a salt-free liquid, and annual maintenance costs will be eight to ten percent of capital costs (four percent is normal). More frequent scheduled shutdowns will be needed for refractory inspection, replacement, and repair. These considerations would also apply for other aqueous salt-solutions such as potassium, magnesium, and calcium salts.

Refractories are mainly aluminum silicates and can be considered to be a fused mixture of aluminum oxide (Al_2O_3) which is basic and silicon dioxide (SiO_2) which is acidic. The sodium salts will be converted in the incinerator to sodium carbonate (Na_2CO_3) which is basic. Sodium carbonate will attack silicon dioxide to form a molten sodium silicate. This will run off, resulting in refractory loss. Sodium attack can be reduced by either using a refractory containing more aluminum oxide or a refractory containing silicon dioxide that has been preheated to a high temperature. The preheating renders the silicon dioxide relatively chemically inert. The process is similar to the "dead burning" of calcium oxide (lime) or magnesium oxide (magnesia) to produce an unreactive material.

These refractories cost about double that of a standard refractory resulting in an increased incinerator cost of about ten percent. Exposure to sodium salts reduces the service life of the

more expensive refractories by about 60 percent (two to four years versus a normal five to ten years). This increases annual incinerator maintenance costs by double or more (eight to ten percent of capital costs compared to a normal four percent).

The more expensive, non-standard refractories are susceptible to process upsets that can shorten refractory life and require more frequent than anticipated refractory changes. The refractory can be damaged by low temperature thermal shock such as would result from spraying liquid solution on the refractory surface, or high temperature excursions where sodium vapor contacts the refractory surface. In the latter case, aluminum oxide undergoes a phase change with the new phase having a different density. The alumina expands, resulting in refractory spallation or flaking. If the oxygen level in the flue gas falls below eight percent, chlorine (from sodium chloride or organic chlorides) can substitute for oxygen in the refractory producing volatile (at incineration temperatures) chlorides resulting in refractory loss.

Refractory damage can be minimized by improved incinerator controls and operator attention:

- Operating temperature should be controlled to $\pm 50^{\circ}\text{F}$ (± 100 to 150°F is normal).
- The operating temperature must never exceed $1,840^{\circ}\text{F}$.
- The oxygen content of the flue gas must be monitored and controlled to be not less than eight percent.
- Temperature changes, while either bringing the incinerator on stream or shutting down the incinerator, must be controlled and at a lower than usual rate.

The more stringent control system would raise incinerator capital costs by about ten percent. Coupled with the ten percent increase generated by a more expensive refractory, an incinerator designed to handle aqueous salt solutions would be about 20 percent more expensive.

Paul Jones of CE Refractories, Valley Forge, Pennsylvania, suggested that in the first year of incinerator operation, the high performance refractory would require replacement due to temperature excursions and upsets resulting from operators being unfamiliar with the incinerator and learning, by experience, how to operate and maintain the incinerator and process instrumentation and controls.

APPENDIX F
CURRENT STATUS OF
ARGONNE NATIONAL LABORATORY PROCESS

PEI ASSOCIATES, INC.

MEMORANDUM

TO: Project File

DATE: August 18, 1989

SUBJECT: Red Water Treatment Technology
Meeting with Argonne National
Laboratory

FROM: J. E. Spessard

FILE: PN 3769-2-C

cc: W. E. Gallagher
T. C. Ponder, Jr.
J. A. Wentz

On August 10, John A. Wentz and John E. Spessard of PEI met with representatives of Argonne National Laboratory's Energy and Environmental Systems Division (ANL). The purpose of the meeting was to: 1) review the progress of ANL's Red Water Treatment Process Development effort, and 2) learn where the group expected to direct future efforts. Representing ANL at the meeting were:

Norman F. Sather, Ph.D., Deputy Director of the division

George F. Vandergrift, Ph.D., Group Leader, Separation Science and Technology Group

L. Reichley-Yinger, Ph.D., Chemical Technology Division

David J. Chaiko, Ph.D., Separation Science and Technology Group

Tenlin S. Tsai, Ph.D., Biochemist

Satya N. Kakar, Microbiologist

Ralph A. Leonard, Chemical Engineer

In their original proposal, ANL intended to separate red water into organic and inorganic fractions through foam fractionation. The organic fraction would contain sodium dinitrotoluene sulfonate salts and other organic compounds associated with TNT manufacturing. This fraction would be microbiologically treated to yield a residue that could either be treated in a conventional plant wastewater treatment system or discharged without further treatment. The inorganic fraction would consist of sodium nitrate, nitrite, sulfate, and sulfite. This fraction would, presumably, be delistable as a hazardous waste.

The ANL group has had very limited success with foam fraction separation and does not intend to pursue it further. Specifics are in their monthly progress reports which I have reviewed in memoranda dated June 15, 1989, and August 7, 1989.

The ANL group now proposes to separate organic and inorganic fractions using polyethylene glycol (PEG) to extract the organic fractions. The PEG would have a molecular weight of 10,000 or higher. Test tube scale experiments have produced organic concentrations in the PEG layer tenfold that of the aqueous layer. This degree of enrichment indicates that a multistage solvent extraction separation of organic and inorganic constituents could be feasible.

The ANL group has tested nine fungi obtained from the Joliet (Illinois) Army Ammunition Plant as well as enzymes obtained from the fungi. The red water was pretreated by freezing or chilling. This precipitates much of the sodium sulfate as Glaubers Salt ($\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$). ANL has identified species that can grow in red water. However, best results have been obtained when glucose was added as a supplemental nutrient. The relative quantities of glucose and red water organics consumed by the fungi and/or enzymes have not been established.

The PEG solvent extraction work has demonstrated that in single stage experiments, red water organic compounds are concentrated in the PEG layer. Essentially, ANL has made a fresh start into separating red water into organic and inorganic fractions. This new approach is in a preliminary stage and minimal progress has been made toward achieving clean separation. Numerous issues must be addressed for this technology to progress past bench scale evaluation. These issues include:

- Extraction efficiencies in second and succeeding stages.
- Relative solubilities of inorganic compounds in PEG and water.
- Solubilities of PEG in water and water in PEG.
- Viscosities in the PEG layer and adapting solvent extraction technology to handle a relatively viscous (compared to water) PEG layer.

The bacteriological work will need to produce a species that digests red water organics. If a supplemental nutrient is required, defining process economics will require that the quantity and identity of the nutrient be determined.

Table F-1 presents a quantitative evaluation of the ANL process based on the five categories of evaluation criteria. The final score for the ANL process is 43 of a possible 110 points.

TABLE F-1. QUANTITATIVE EVALUATION OF ARGONNE NATIONAL LABORATORY PROCESS

	<u>Points awarded</u>
1. Theoretical potential for red water treatment	5
2. Current application and status of technology	6
3. Environmental impact	26
Wastewater discharge regulations	3
Air emission regulations	9
Solid/hazardous waste regulations	14
Recyclability	0
4. Time and cost for implementation	3
Time	2
Cost	1
5. Complexity, operation, and flexibility	3
Process complexity	1
Difficulty of operation	1
Flexibility of operating parameters	1
Miscellaneous	0
TOTAL	43

APPENDIX G

MEMORANDUM DESCRIBING CONTACTS MADE CONCERNING
RED WATER PROCESSING AT
DUPONT'S DEEPWATER, NEW JERSEY, FACILITY

PEI ASSOCIATES, INC.

MEMORANDUM

TO: Project File

DATE: July 17, 1989

SUBJECT: Radford Army Ammunition Plant
Red Water Treatment at DuPont's
Deepwater, New Jersey, Facility

FROM: J. E. Spessard *JS*

FILE: PN 3769-2-C

cc: W. E. Gallagher
T. C. Ponder, Jr.
J. A. Wentz

At the red water meeting in Cincinnati on July 12, several questions were raised about the option of shipping red water to DuPont for contract disposal. Specifically, is DuPont really willing to treat the waste and are they permitted to take K047 wastes? The second level evaluation is almost complete, and this memo will address the questions prior to the release of the second level evaluation. Conversations we have had about delisting red water are also discussed. While we only discussed delisting red water, chances would probably be better if the red water were pretreated; for example, by wet air oxidization to remove most of the organics.

Contract Disposal at Deepwater

The following information was developed regarding shipping red water to DuPont for disposal:

- B. Z. Miller of DuPont (see attached letter) quoted 32 cents per gallon for treating red water (the 32-cent rate is significantly lower than the 60-cent rate quoted James Morris of Hercules in 1983). A copy of Mr. Miller's letter giving the quotation is attached. I had sent Mr. Miller a copy of the RAAP red water analysis.
- Ed Spurling of the Norfolk and Southern Railroad quoted a budgetary freight rate of \$1.75 per 100 pounds, about 16 cents per gallon.
- Gary Meyers of Trinity Industries quoted \$70,000 each for 30,000 gallon capacity railway tank cars.

Al Pagano of DuPont had told me in February 1989 that the Deepwater facility was licensed to accept K047 wastes.

Ron Sharp of the Norfolk and Southern Railroad told me on May 29, 1989, that DuPont's wastewater treatment facility at Deepwater had available capacity and that DuPont was looking for outside customers. This may explain the lower rate quoted me than quoted Jim Morris in 1983.

On May 15, 1989, I telephoned the New Jersey Division of Hazardous Waste Management. My objectives were:

- To verify that DuPont was permitted to handle K047 wastes;
- To learn the compliance record and status of the Deepwater facility in general and the wastewater treatment plant in particular; and
- To learn if there would be any problems with a New Jersey facility handling and treating RCRA hazardous wastes generated in another state.

The lady who answered the telephone recommended that I put my inquiries in writing. A copy of my letter to Thomas Downey of the New Jersey Division of Hazardous Waste Management is attached.

The New Jersey Department of Environmental Protection (DEP) responded to my letter by a telephone call from Terry Ostrander of DEP (609/346-8002) on June 2, 1989. Mr. Ostrander told me:

- DuPont was authorized to receive K047 wastes and it would be acceptable to New Jersey to send red water to Deepwater.
- The State finds violations at Deepwater but not severe violations. Typical violations would be manifests, labeling, and drum handling. The violations would be typical of a facility of this size.
- The only present unresolved compliance issue is that the State contends that DuPont's analytical laboratory should be running analysis for additional organic compounds. Mr. Ostrander said that this had been an issue for two years and DuPont and the State were working to correct the situation. I felt that Mr. Ostrander did not consider this a serious problem.
- The State inspects the Deepwater facility weekly, spending about three man-days per week at the site.

To summarize, the New Jersey Division of Hazardous Waste Management finds red water treatment by DuPont to be acceptable.

Red Water Delisting

On May 16, 1989, I spoke with Terry Grist of the U.S. EPA (202/382-4782) concerning the possibility of getting RAAP red water delisted as a hazardous waste. At that time, I was unaware that Hercules had attempted to get RAAP red water delisted in 1985 or 1986 and had been turned down because the VMS Groundwater Mathematical Model had indicated a potential for groundwater contamination.

Mr. Grist indicated that RAAP red water was potentially delistable and that the Lake City Army Ammunition plant had petitioned for delisting their red water (their red water is actually a "pink" water).

Mr. Grist pointed out that K047 wastes are classified hazardous due to reactivity and not due to the presence of any specific compound. He emphasized that if you combine a RCRA hazardous waste so classified because of a property (reactive, corrosive, toxic, ignitable), and mix it with a solid waste so that it no longer exhibits the characteristic, it is delistable.

Mr. Grist told me that there is a guidance document for the delisting procedure available through the National Technical Information Service. He outlined the delisting procedure:

- Establish what is in the waste.
- Establish that the waste is not reactive, corrosive, toxic or ignitable.
- Establish that there are no 40 CFR 261 Appendix 8 constituents.

EPA would review the application and if the application for delisting was accepted, EPA would publish the decision in the Federal Register. After accepting public comments, EPA would issue a finalized decision. The process would require 12 to 18 months.

EPA could require testing for the presence of specific 40 CFR 261 Appendix 8 compounds if there was reason to suspect their presence. Jim Morris pointed out that RAAP red water contained trace amounts of 2,4- and 2,6-dinitrotoluene and 1,3,5-trinitrobenzene, which are 40 CFR 261 Appendix 8 compounds.

The presence of Appendix 8 compounds does not, of necessity, classify a waste as RCRA hazardous. 40 CFR 261.11(a)(3) lists the steps that EPA may take to classify such a waste as non-hazardous. However, in 1985 or 1986, the parties who represented EPA in evaluating RAAP red water determined that RAAP red water was a hazardous waste and refused to declassify it.



ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

WILMINGTON, DELAWARE 19898

CHEMICALS AND PIGMENTS DEPARTMENT

Technical Laboratory (D)
Chambers Works
Deepwater, New Jersey 08023

April 26, 1989

Dr. John E. Spessard
PEI Associates, Inc.
1006 North Bowen Road
Arlington, TX 76012

Dear Dr. Spessard:

In response to your request of March 31, 1989:

We estimate the treatment cost for "red water" from the Radford, Virginia, Arsenal to be \$.038/pound or \$.32/gallon. This is an approximate estimate for budgetary purposes only and is subject to confirmation and acceptance following sample analysis.

In order to qualify for treatment at our facility, we ask that you submit a one-pint sample accompanied by a completed questionnaire (enclosed). We will analyze the sample for pricing and compatibility with our treatment facility. At that time, we will submit a formal quotation.

We appreciate your consideration of Du Pont for your disposal needs. Should there be any questions, do not hesitate to call me.

Very truly yours,

B. Z. Miller
(609) 540-2727

BZM:nep
Enclosure
05724

DU PONT WASTEWATER TREATMENT SERVICE

WASTE CHARACTERIZATION QUESTIONNAIRE Date: _____ Du Pont Sample I.D. No. _____

■ Waste Generator

Company Name _____ Phone _____

Address _____

City _____ State _____ Zip _____

Contact _____

■ Submitter of Sample if Different from Generator

Company Name _____ Phone _____

Address _____

City _____ State _____ Zip _____

Contact _____

■ Process Generating Waste _____

■ If RCRA listed, give EPA Hazardous Waste No. _____

■ Dot Hazard Class _____

■ Attach a typical analysis of your wastewater.

■ Composition and Classification Information

Major Components	EPA Hazardous Waste No.	Concentration %	
		Upper	Lower
1. _____	_____	_____	_____
2. _____	_____	_____	_____
3. _____	_____	_____	_____
4. _____	_____	_____	_____
5. _____	_____	_____	_____

pH _____ Specific Gravity _____ ☐ Heavy Metals (Specify) _____

PLEASE CIRCLE YES (Y) OR NO (N) TO THE PRESENCE OF THE FOLLOWING MATERIAL CHARACTERISTICS OF THE WASTE:
Water Solution Y/N, Water Dispersion (Emulsion) Y/N, Corrosive Y/N, Carcinogen or Suspect Y/N, Poison Y/N,
Oxidizer Y/N, Explosives Y/N, Radioactive Y/N, PCB's Y/N, Asbestos Y/N, Cyanide Y/N, Sulfides Y/N,
Pesticides-Herbicides Y/N,

Flash Point _____ TOC _____ BOD _____ COD _____ Odor ☐ Yes ☐ No

☐ Reacts with Acidic Water _____ ☐ Products of Reaction _____

Volume of Material: Gallons Per Month _____

Handling Precautions _____

☐ Sample Size — Please send a one pint sample in a polyethylene or polypropylene bottle sealed with a screw cap of similar material for analysis and pricing.

☐ Questionnaire Completed By (Name) _____

DU PONT COMPANY • CHEMICALS & PIGMENTS DEPARTMENT
CHAMBERS WORKS • TECHNICAL LAB SPOT 746 • DEEPWATER, NJ 08023
PHONE (609) 200-5100

DU PONT

SAMPLE NO. D _____ LOG BOOK _____
CUSTOMER _____

RECEIVED _____
COMPLETED _____

ENVIRONMENTAL SERVICES LABORATORY
OUTSIDE WASTE ANALYTICAL SHEET

pH _____

ODOR _____

Sp.G. _____

COMPUTER PRICE _____

COMBUSTIBILITY Y/N

WATER MISCIBLE Y/N

LATEX TEST PASS/FAIL

REMARKS _____

EBOD

REGULAR _____	H.M. _____
4 HR _____	_____
8 HR _____	_____
12 HR _____	_____
16 HR _____	_____
20 HR _____	_____

SPECIAL ANALYSIS

TOTAL S ²⁻ _____	ARSENIC _____
SOLBL S ²⁻ _____	COPPER _____
CYANIDE _____	LEAD _____
TOTAL Cr _____	MERCURY _____
Cr ⁶⁺ _____	NICKEL _____
	ZINC _____
	OTHERS _____

ACID mg/l _____
$$\frac{(\quad) \times N \times 50.000}{S}$$

BASE mg/l _____
$$\frac{(\quad) \times N \times 50.000}{S}$$

NEUTRALIZATION DILUTION FACTOR — NDF

$$NDF = R \times \left(1 + \frac{A}{V}\right)$$

DOC mg/l _____
NDF _____
OTHER _____

TSS mg/l _____
$$\frac{G - T \times NDF \times 1,000,000}{V}$$

G —
T —
N —

PEI ASSOCIATES, INC.

1006 N. BOWEN ROAD
ARLINGTON, TEXAS 76012
(817) 460-0777

May 18, 1989

Mr. Thomas Downey
New Jersey Division of
Hazardous Waste Management
20 East Clementon Road
Gibbsboro, New Jersey 08026

Reference: PN 3769-2-C

Dear Mr. Downey:

I have briefly discussed this request on May 15, 1989, with the lady who answers the telephone. She recommended that the request be submitted to you by letter.

The U.S. Army is considering reopening the mothballed Radford, Virginia TNT plant. The waste water from TNT production, or red water, is classified as RCRA Hazardous (K047). This classification is due to reactivity rather than any particular constituent.

When the plant previously operated, red water was sold to a paper mill. Paper mill technology has changed and this would no longer be an option. While there is no satisfactory red water treatment technology published in the open literature, several chemical plants produce dinitrotoluene which also has a waste stream called red water. Common to all of these plants is that they treat their red water, they appear to be in compliance, and the technology is classified by the company as proprietary.

Consequently, I contacted dinitrotoluene manufacturers to learn if any would be interested in either treating Radford red water or in licensing their technology. Of those contacted, DuPont has been by far the most responsive. DuPont has provided a budgetary quotation for treating red water at Deepwater.

DuPont has told me that they have an existing permit to handle K047 wastes. The DuPont proposal seems attractive and I am very interested in the compliance status and record of the Deepwater facility in general and particularly the wastewater treatment facility.



CHESTER TOWERS

CORPORATE OFFICE

11409 CHESTER ROAD
CINCINNATI, OHIO 45246
(513) 782-4700

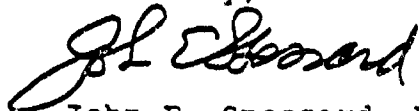


An analysis and physical properties of Radford red water are enclosed. The red water volume would be 16,500 gallons per day. However, to reduce freight charges, the volume might be halved by increasing the solids content from 15 to 30 percent. This would be accomplished by evaporation at Radford.

I have contacted the Norfolk and Southern Railroad which serves Radford. The red water would be loaded onto Army-owned or leased tank cars at Radford. The tank cars would be transferred from the Norfolk and Southern to Conrail at the Lynchburg, Virginia South Potomac Yard, and from there carried to Deepwater by Conrail. Empty cars would be returned by the same route.

If you have any questions, please call me at (817) 460-0777. Your response will be appreciated.

Sincerely,



John E. Spessard, Ph.D.

JES:car

cc: T. C. Ponder, Jr.

RED WATER MAKEUP

- Red water characteristics vary continuously.
- No U.S. TNT production facility is in production at this time.
- No Red Water samples are available.
- Nominal constituents of Radford AAP are:

Percent Solids:	15% nominal
Water Content:	85% nominal
pH:	7.0 - 9.7
Color:	Dark Red
Specific Gravity:	1.1 nominal
Dry Solids:	Will burn
Solids heat value:	Variable (3200 BTU/lbm nominal)
Metal Content:*	
Calcium	346 mg/l
Iron	307 mg/l
Magnesium	90 mg/l
Potassium	42 mg/l
Aluminum	10 mg/l
Chromium	4.94 mg/l
Barium	3.0 mg/l
Copper	2.30 mg/l
Cadmium	0.66 mg/l
Silver	0.40 mg/l

- * Nominal values obtained from EP Toxicity Testing.

RAAP RED WATER SOLIDS

Inorganic Salts

$\text{Na}_2\text{SO}_3\text{-Na}_2\text{SO}_4$
 NaNO_2 (sodium nitrite)
 NaNO_3 (sodium nitrate)
 Sodium sulfide ($\text{NaHS-Na}_2\text{S}$)
 Sodium carbonate/bicarbonate

Percent by Weight

32.3 ——— 10.46
 11.2 ——— 3.73
 1.5 ——— 0.37

May be present

May be present

45.0

Nitrobody

Sodium sulfonate of 2,4,5-TNT
 Alpha-TNT-Sellite complex
 Sodium sulfonate of 2,3,4-TNT
 Sodium sulfonate of 2,3,6-TNT
 Sodium sulfonate of 2,3,5-TNT
 2,4,6-TNBA (trinitrobenzoic acid) sodium salt
 White compound sodium salt
 TNBAL-bisulfite addition compound
 (trinitrobenzaldehyde)
 TNBOH (trinitrobenzyl alcohol)
 Sodium nitroformate
 3,4-DNBA (dinitrobenzoic acid) sodium salt
 2,3-DNBA (dinitrobenzoic acid) sodium salt
 TNB (trinitrobenzene-Sellite complex)
 Dissolved 2,4-DNT (dinitrotoluene)
 Dissolved a-TNT (trinitrotoluene)

22.7 4.52

16.2

9.6

2.0

Trace

1.0

1.0

1.0

1.0

0.5

Trace

Trace

Trace

Trace

Trace

55.0

100.0